

Report No. SFIM-AEC-ETD-CR-95036 Final Report

Pink Water Treatment Options



May 5, 1995 Contract No. DAAA 21-93-C-0046 Task No. 0015

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Pink Water Treatment Technology

Final Report

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LIST OF TERMS

<u>Term</u>	<u>Definition</u>
\$	U.S. dollars
°F	temperature, degrees Fahrenheit
OH.	hydroxyl radical
1990 Amendments	Clean Air Act Amendments of 1990
AAP	Army Ammunition Plant
anon	anonymous
AOP	advanced oxidation process
AST	atomized suspension technique
BLCC	Building Life Cycle Cost
BOD	biochemical oxygen demand
CAA	Clean Air Act
CE Index	chemical engineering plant cost index
CERCLA	Comprehensive Environmental Response Compensation
CERCLA	Liability Act
CED	Code of Federal Regulations
CFR	Center for Hazardous Materials Research
CHMR	carbon dioxide
CO ₂ COD	chemical oxygen demand
CPI	Consumer Price Index
CWA	Clean Water Act
DDT	dichloro-diphenyl trichloroethane
DNB	dinitrobenzene
DNT	2,4-dinitrotoluene
DOD	Department of Defense
DOE	Department of Energy
DSPB	dual shell, pressure balanced
EBP	electron beam process
EPA	Environmental Protection Agency
FBR	fluidized bed reactor
FOTW	federally owned treatment works
GAC	granular activated carbon
gpm	gallons per minute
gpy	gallons per year
H°	hydrogen radical
H_2O_2	hydrogen peroxide
HA	Drinking Water Health Advisories
HAP	hazardous air pollutant
HMX	cyclotetramethylene-tetranitramine
HSWA	Hazardous and Solid Waste Amendments
LAP	load, assemble, and pack
lb	pound(s)
LCC	life cycle cost
	•

<u>Term</u> <u>Definition</u>

LDR land disposal restriction

mA $1x10^{-3}$ Amperes

MAAP Milan Army Ammunition Plant

MACT maximum achievable control technology

μg/m³ micrograms per cubic meter

mg milligrams

mg/l milligrams per liter
MIOX mixed oxidant
MW molecular weight

NAAOS national ambient air quality standards

NDCEE National Defense Center for Environmental Excellence NESHAP national emission standards for hazardous air pollutants

NH₃ ammonia

NitRem nitrogen removal process

nm nanometers

NO_x oxides of nitrogen

NPDES National Pollutant Discharge Elimination System

 O_3 ozone

PACT powdered activated carbon treatment

PAT plasma arc technology PCB polychlorinated biphenyl

POTW publicly owned treatment works

ppm parts per million

psi pounds per square inch

RCRA Resource Conservation and Recovery Act

RfD Reference Doses

RDX cyclotrimethylene-trinitramine

RO reverse osmosis

SCWO supercritical water oxidation SDWA Safe Drinking Water Act

SEX monoacetyl derivative of HMX

TiO₂ titanium dioxide
TNB trinitrobenzene
TNT trinitrotoluene
TOC total organic carbon

TSD treatment, storage, or disposal

TTC total treatment cost

USAEC U.S. Army Environmental Center

UV ultraviolet

VOC volatile organic compound

WAO wet air oxidation wt % weight percent

EXECUTIVE SUMMARY

Origin and Composition of Pink Water

Army Ammunition Plants (AAPs) perform two functions that generate a waste stream known as pink water. These functions are (1) load, assemble, and pack (LAP), and (2) demilitarization of munitions. Associated housekeeping and processing operations, for example, wash down and wash out of munitions, and laundering workers' clothing, create the waste water stream. Pink water typically contains trinitrotoluene (TNT), which is photochemically active, resulting in the color giving pink water its name. In addition, pink water usually contains cyclotrimethylene-trinitramine (RDX) and cyclotetramethylene-tetranitramine (HMX). The composition of pink water is highly variable, dependent on process materials and operations. 200 ppm dissolved energetic related materials is the reference value used in this work. By law, pink water must be in compliance with discharge limits before disposal.

Objective: Evaluate Alternatives to Current Treatment Technology

Currently, AAPs meet discharge requirements by using carbon adsorption to remove contaminants from pink water. The carbon is then either regenerated for reuse or incinerated for disposal. More effective technologies are being sought for pink water treatment. The objective of this task is to evaluate alternatives to the current activated carbon treatment of pink water, and to select five of these technologies for further evaluation.

Regulatory Requirements

This report identifies regulatory issues that should be considered in the evaluation of alternative treatment technologies for pink water. The discharge of contaminated wastewater is a primary concern for AAPs. AAPs generating pink water must comply with all applicable wastewater effluent limitations before pink water wastes can be discharged. Current discharge limits for total nitrobodies at Crane, Kansas, Lonestar, and Milan AAPs are identified in this report. Also, because some observers have noted that discharge limitations for nitrobodies appear to be heading in the direction of the more stringent standards set for groundwater, this report identifies the current U.S. EPA Drinking Water Health Advisories for chemicals found in the pink water. While these Health Advisories are not binding, state and local agencies often look to them for guidance when establishing groundwater treatment standards.

The treatment of pink water often results in the generation of hazardous waste. For this reason, applicable hazardous waste management and disposal requirements are also included. Finally, there has been a great deal of recent regulatory activity relating to the implementation of the Clean Air Act Amendments of 1990. These regulatory issues are also considered.

Alternative Technologies

This report evaluates potential methods for treating pink water, comparing these technologies against the standard of granular activated carbon (GAC) treatment followed by either off-site thermal destruction or regeneration. Alternative processes were classified into two categories, separation and destruction technologies.

The principal separation technologies evaluated are: 1) resin adsorption, 2) surfactant complexing, 3) liquid-liquid extraction, 4) powdered activated carbon, 5) carbon adsorption with regeneration, 6) ultrafiltration and 7) reverse osmosis. Because separation technologies require additional processing to destroy the contaminants, technologies that destroy these compounds directly are more advantageous. In addition, separation technologies may not be compliant with increasingly stringent environmental regulations.

This report reviews more than 27 different destruction technologies relevant to pink water treatment. Of these technologies, 16 passed preliminary criteria screening for reasonableness, and had adequate data to permit life-cycle cost analysis. These technologies are listed without further comment in Table ES-1.

Table ES-1
Destruction Technologies Reviewed

Technology	Technology	Technology
Base catalyzed hydrolysis	Wet air oxidation (WAO)*	Anaerobic expanded-bed GAC
Advanced oxidation process, Vendor A*	Supercritical water oxidation (SCWO), Vendor A*	Anaerobic fluidized bed GAC*
Advanced oxidation process, Vendor, B*	Supercritical water oxidation (SCWO), Vendor B*	Anaerobic-aerobic fluidized bed GAC
Fenton's chemistry*	GAC with Supercritical water oxidation*	Aerobic GAC cycling batch thermophilic bioreactor*
Mono-persulfate and H ₂ O ₂	NitRem process*	Aerobic rotary biological contactor
Ultraviolet and TiO ₂	Plasma arc technology	Algal turf scrubbing
Ultraviolet and O ₃	Gas-phase hydrogen reduction	Mixed microbial mats
Electrolytic, Vendor A*	Electron beam, Vendor A*	Large aquatic plants (weeds)*
Electrolytic, Vendor B*	Electron beam, Vendor B*	Enzymatic treatment
		Combinations, biological with carbon and WAO*

^{*} Passed preliminary reasonableness screen and analyzed for life-cycle costs.

Evaluation Methods

The most promising separation and destruction technologies for pink water treatment were evaluated and compared. Process costs were compared on the basis of treating 20 gpm pink water containing 200 ppm contaminants. Capital and operating cost data were obtained from published and unpublished sources, e.g. equipment manufacturers, vendors, and technology owners. Using these data, a total treatment cost was calculated for each process. Either direct or in situ destruction is recommended, rather than a separation process followed by secondary, off-site destruction.

Technology evaluations were based on the following criteria: 1) total life-cycle cost, 2) effluent quality, 3) process operability, 4) flexibility (technology mobility, ease of start up and shut

down), 5) health and safety (process hazards analysis and safety review), and 6) commercial availability. The selection criteria were weighted to emphasize economics and effluent quality, 35% and 25%, respectively. Process operability was weighted 15%. Process flexibility and health and safety were weighted 10%. Commercial availability was weighted the least, namely 5%.

Conclusions

Total scores, derived from weighted selection criteria, ranked the technologies shown in Table ES-1. The most effective pink water destruction processes are:

- 1. Large aquatic plants (Biological destruction)
- 2. GAC thermophilic process (Biological destruction)
- 3. Fenton's chemistry (Chemical oxidation)
- 4. Electrolytic system (Electrolytic oxidation)
- 5. Fluidized bed bioreactor (Biological destruction).

The first three processes clustered in overall score and were differentiated from the bottom group. Process economics for all of these technologies were similar to the current GAC treatment costs. Quantification of effluent toxicity is a priority need for all future work.

Recommendations

A bench-scale test program to evaluate at least five technologies is recommended. The technologies should be tested with identical pink water samples to enable relative performance comparisons. Both LAP plant pink water and demilitarization operations pink water should be tested. Process testing should be conducted by technology owners at one LAP plant. The permitting issues should be addressed as soon as possible. Effluent toxicity should be a primary measurement for every technology. After bench scale testing, three of the five processes should be selected for pilot-scale testing, if they satisfy performance requirements.

1.0 INTRODUCTION

1.1 Origin of Pink Water

Pink water, a waste stream, results from two functions, load, assemble, and pack (LAP) and munitions demilitarization. The waste stream is produced at Army Ammunition Plants (AAPs) from wash down, wash out, and laundering of workers' clothing. Wash down is the washing of munitions and facilities after the LAP steps. Wash out is the flushing of explosives from munitions during demilitarization. AAPs have significantly reduced the amounts of pink water being generated. For example, instead of using hot water wash outs, dry vacuum recovery systems are applied to collect solids. This pollution prevention step greatly reduces the amount of pink water that must be treated before disposal.

1.2 Composition

Pink water contains toxic nitrobodies such as: trinitrotoluene (TNT), cyclotrimethylene-trinitramine (RDX), cyclotetramethylene-tetranitramine (HMX), and related compounds. Typical analyses of pink water from various sources are given in Table 1-1.

Pink water composition varies widely between different production and demilitarization facilities, depending on the munitions being processed. However, the common feature of these waste streams is the pink color, due to the photochemically active TNT. This forms colored compounds when exposed to light. Because of increased environmental awareness, federal, state, and local regulations mandate removal of these toxic compounds before the process effluent can be discharged to federally owned treatment works (FOTWs) or local waters such as streams, lakes, and rivers.*

^{*}To demonstrate the far reaching effects of regulations, a regulatory analysis of the current discharge limits and anticipated future changes to these limits at four AAPs (Kansas, Lone Star, Crane, and Milan) are presented in Section 2.0.

Table 1-1
Average Filtered, Pre-Carbon Treated Pink Water Compositions and Flow Rates From Various Load, Assemble, and Pack Operations

Source*	A^{I}	B^I	C^2	D^3
Flow rate, gpy	237,000	1,133,000	71,800	N/A
Component		Concentrat	ions, ppm	
TNT	< 0.004	25.61	34.0	112
RDX	1.92	20.29	11.0	76
HMX	0.60	2.19	1.3	11
2,4-dinitrotoluene (DNT)	<0.005	0.15	10.0	1
trinitrobenzene (TNB)	<0.003	0.27	0.36	5
2.6-DNT	< 0.005	0.08	0.19	Trace
dinitrobenzene (DNB)	N/A**	N/A	N/A	Trace
monoacetyl derivative of HMX (SEX)	N/A	N/A	N/A	1
TOTAL NITROBODIES	2.54	48.59	56.85	206

^{*} Numbers refer to references listed in Section 9.0

1.3 Pink Water Toxicity and Discharge Limits

TNT has been known to be toxic to humans and the environment for some time. The first signs of TNT poisoning in humans are hematological changes, which can result from both chronic and acute exposure to TNT in any form. Reduction of red blood cell count and hemoglobin content may be associated with chemical and physical changes in the blood. Pink water toxicity depends on concentration. A source indicates that discharge limits may be lowered to 10 parts per billion (ppb). This possible 10-ppb limit is a cause for concern in terms of cost and benefit.

1.4 Present Treatment

Granular activated carbon (GAC) adsorption is currently the standard technology for treating pink water, and maintaining discharges within limits. Explosive-laden GAC requires either regeneration or destruction. Off-site thermal regeneration is commonly used. In addition to regeneration, explosive-laden GAC is burned as

^{**} N/A denotes no data available.

Note: AAPs are operating below capacity, so full mobilization flow rates should be higher. However, with the implementation of more pollution prevention technologies, or by increasing water recycle, these flow rates could dramatically decrease.

[†]Current discharge limits are given in Table 2-1.

fuel in boilers and cement kilns. Scrubbers installed on incineration equipment reduce air pollution. However, incineration is expensive, permitting can be difficult, and scrubber waste water can be problematic.

1.5 Task Objective

The objective of the current work is to evaluate alternatives to the current GAC treatment of pink water, and to select five of these technologies for further evaluation. These alternatives consist of separation and destruction technologies. As called for in the statement of work, the five leading candidate processes were selected using the following evaluation criteria:

- Total life-cycle cost of the process (capital and operating costs)
- Effluent quality
- Process operability
- Process flexibility
- Health and safety factors
- Commercial availability.

1.6 Report Organization

This report starts with a regulatory analysis, because compliance is the driving force for change and the guidance for technical requirements. Sections describing separation and destruction technologies follow. Each feasible destruction technology description is followed by a graphic which compares the candidate process to the current GAC process. After the technology descriptions, the details of the evaluation methods are explained, Section 5. Evaluations are performed and results are discussed in Section 6. Finally, the report closes with conclusions and recommendations, Sections 7 and 8. References are contained in Section 9. The appendix contains details of the capital and operating cost data for the technologies evaluated.

2.0 REGULATORY ANALYSIS

Like many other process waste streams, pink water is regulated by federal, state, and local environmental agencies. The pink water constituents of primary regulatory concern are toxic nitrobodies, e.g., TNT, RDX, HMX, 2,4-DNT, and DNB.

A regulatory analysis was performed focusing on the wastewater, hazardous waste, and air emission regulations at four AAPs. These plants are: Crane AAP, Crane Indiana; Kansas AAP, Parsons Kansas; Lone Star AAP, Texarkana Texas; and Milan AAP, Milan Tennessee. Environmental regulatory constraints have been increasing in scope of coverage and stringency over recent years, and this trend is expected to continue in the future. Whenever possible, anticipated future changes to the regulations have been included.

2.1 Wastewater Regulations

Of the AAPs surveyed, only one, Milan AAP (MAAP), discharges directly to surface waters. At MAAP, waste waters are discharged directly into "drainage ditches" after being treated to discharge limits specified in its national pollutant discharge elimination system (NPDES) permit. The other three AAPs discharge their treated waste waters into host installation sewage systems (i.e., FOTWs). As indirect dischargers, these AAPs are not required to obtain NPDES permits themselves, but the sewage treatment facilities that receive their discharges must obtain NPDES permits. As such, each sewage treatment facility has its discharge limits set in an individual NPDES permit. To meet their discharge limits, the sewage treatment facilities place specific pretreatment limits on the AAPs.

In addition to any location-specific pretreatment limits, indirect dischargers must also comply with the general pretreatment regulations found in 40 Code of Federal Regulations (CFR) part 403 et seq. These general pretreatment requirements are designed to prevent the discharge of pollutants that would interfere with the operation of the sewage treatment system, and prevent the discharge of pollutants that would pass through the treatment works without receiving adequate treatment.

All applicable pretreatment limits must be met before any discharges can be made to the sewage treatment system. This is accomplished by treating the pink water, at industrial wastewater treatment facilities located at each plant, before making any discharges to the host installation sewage system. To meet their discharge limits, summarized in Table 2-1, all four AAPs currently use GAC to treat pink water.

Table 2-1
Current Discharge Limits for Total Nitrobodies
for Four Army Ammunition Plants*

AAP	Nitrobodies	Discharge Limits (ppm)
Crane	Total Nitrobodies	2.0 (Daily Average)
Kansas	Cyclonite (RDX)	0.5 (Daily Average)
		1.0 (Daily Maximum)
	Trinitrotoluene (TNT)	0.5 (Daily Average)
		1.0 (Daily Maximum)
Lone Star	Trinitrotoluene (TNT)	0.3 (Daily Average)
		1.0 (Daily Maximum)
	Cyclonite (RDX)	15 (Daily Average)
		25 (Daily Maximum)
Milan	Total Nitrobodies	0.1 (Daily Average)
	Total Nitrobodies	0.5 (Daily Maximum)

^{*}As specified by individual permits.

No federal uniform limitations currently exist to regulate the discharge of nitrobodies from operations involved in the LAP and demilitarization of munitions. In 40 CFR part 457, subpart C, discharge limitations have been established for the Explosives LAP Plants Subcategory of the Explosives Manufacturing Point Source Category. These limitations were established in 1976 for direct dischargers (i.e., those requiring NPDES permits such as Milan). These limitations do not, however, include specific limitations for nitrobodies. The pollutants specifically covered by these limitation guidelines are oil and grease, total suspended solids, and pH.

Because there are no applicable federal, uniform discharge limitations for pink water from AAPs, discretion is left to state and local agencies to establish discharge limitations. The lack of national limitations explains the different discharge limitations faced by each of the four AAPs surveyed for this report. When discharge limitations are established for a facility, the main factors that regulatory agencies take into consideration are: the quality of the body of water receiving the wastewater discharges, the designated uses (for example, drinking water use or recreation use) for that water body, and the ability of the water body to assimilate pollutants.

The U.S. Environmental Protection Agency (EPA) has issued water quality criteria for certain pollutants. TNT and RDX are not specifically addressed, but for 2,4-DNT, the human health-based water quality criterion has been set at 0.11 parts per billion (ppb), for water and fish. The 2,4-DNT levels at which there are no observed effects are: 330 ppb fresh water acute, and 230 ppb fresh water chronic.⁶

2.1.1 Groundwater Standards

Some observers have indicated that discharge limitations for nitrobodies appear to be moving closer to the standards established for nitrobodies in groundwater. Typically, groundwater standards are established in the context of a site remediation. When contaminated groundwater is pumped and treated during remediation, treatment standards are usually established for the groundwater contaminants. These standards are generally arrived at on a case-by-case basis using risk assessment techniques that ask questions about the site's future intended use, the risks from exposure to the contaminants, and the uses of the neighboring land.

States will often look to relevant drinking water standards [maximum contaminant levels (MCLs)] for guidance when setting groundwater standards, but the final decision will ultimately rest on the circumstances of the site. No federal MCLs exist for nitrobodies, but there have been some relevant Drinking Water Health Advisories (HAs) issued by EPA for 2,4-DNT, HMX, RDX, and TNT. For example, the Reference Doses (RfD) and Lifetime HAs for a 154 pound adult are given in Table 2-2.

Table 2-2
Reference Doses and Lifetime Health Advisories of Pink Water
Constituents for a 154 Pound Adult⁷

Chemicals	RfD, (ppm/day)	Lifetime HA (ppm)
2,4-DNT	0.002	
HMX	0.05	0.4
RDX	0.003	0.002
TNT	0.0005	0.002

RfDs, expressed in ppm/day, represent an "estimate of a daily exposure to the human population that is likely to be without appreciable risk of deleterious effects over a lifetime." Lifetime HAs, expressed in ppm, represent "the concentration of a chemical in drinking water that is not expected to cause any adverse non-carcinogenic effects over a lifetime of exposure, with a margin of safety."

While these HAs are not binding, states may use them for guidance in setting groundwater standards. Again, it is a state-by-state, case-by-case decision. In Indiana, for example, the state has established groundwater cleanup goals for 2,4-DNT as part of its Voluntary Remediation Program. At a site being restored under this program for industrial re-use, a cleanup goal of 0.204 ppm has been established. For sites being restored to residential use, the groundwater cleanup goal for 2,4-DNT has been set at 0.0608 ppm.⁸

2.1.2 Clean Water Act Reauthorization

Just as the current regulations differ by site, future regulations are also likely to vary by site unless EPA rewrites the source category guidelines to specifically include effluent limitations for nitrobodies in the effluent limitation guidelines for the Explosives Manufacturing Point Source Category, Subpart C: Explosives LAP Plants Subcategory, of the Clean Water Act (CWA). While EPA is currently reviewing a number of source category effluent limitation guidelines, the Explosives Manufacturing Point Source Category is not one of them.

More likely, however, AAPs will face more stringent regulations based on the anticipated reauthorization of the CWA. Among the issues addressed by the reauthorization bills currently under consideration by Congress are: watershed protection, revised water quality criteria, greater control of toxic pollutants, effluent guidelines and pretreatment standards, increased emphasis on pollution prevention planning, and stricter enforcement. Emphasis on watershed protection and more stringent water quality criteria are both issues likely to drive down the discharge limits for nitrobodies in pink water streams. CWA reauthorization may occur during the 104th Congress.

2.2 Hazardous Waste Regulations

Wastes qualifying as "hazardous" under given regulatory and statutory definitions must be managed and ultimately treated, stored, or disposed of in accordance with Subtitle C of the Resource Conservation and Recovery Act (RCRA). In general, wastes will be classified as hazardous if they meet the broad definition of solid waste and they also either: 1) exhibit one of the four characteristics of hazardous wastes (i.e., ignitability, corrosivity, reactivity, or toxicity), or 2) are listed as hazardous by regulation.

Under the "Hazardous Wastes from Specific Sources" list, three listings are found that are relevant to AAPs where the LAP and demilitarization of munitions takes place. These listings are given below by their industry and the EPA's hazardous waste number, along with a description of the included wastes:

K044	Waste water treatment sludges from the manufacturing
	and processing of explosives.
K045	Spent carbon from the treatment of waste water
	containing explosives.
K047	Pink/red water from TNT operations.

Pink Water Treatment Options

These three listings have received the "Reactive Waste (R)" Hazard Code as the basis for their hazardous waste listing.

Proper management of hazardous wastes requires compliance with applicable on-site storage limits, manifesting, record keeping, and reporting requirements. If a facility's waste meets the description of a listed hazardous waste, but does not meet any of the criteria under which the waste was listed as hazardous (i.e., reactivity for K045 listed wastes), the facility can petition EPA to "delist" its particular waste (40 CFR §260.22). By regulation, a listed hazardous waste not meeting any of the criteria under which the waste was listed as hazardous, still cannot be delisted unless the "petitioner also ... demonstrate[s] that this waste does not exhibit any of the hazardous waste characteristics, as well as present[s] sufficient information for the Agency to determine whether the waste contains any other toxicants at hazardous levels" (51 Fed. Reg. 33628, September 22, 1986). Because of this requirement, AAPs must test their listed wastes not only for reactivity but also for the hazardous waste characteristics of toxicity, ignitability, and/or corrosivity when filing delisting petitions. If the waste tests positive for any one or more of these characteristics, then it cannot be delisted.

For determining whether a waste exhibits the toxicity characteristic, EPA has established maximum concentrations (regulatory levels) for a number of toxic contaminants at 40 CFR §261.24 (see Table 1 in 40 CFR). Wastes must be treated as exhibiting the toxicity characteristic if they contain any of the listed contaminants at levels equal to, or in excess of, the given maximum concentration. EPA has set a maximum concentration level of 0.13 ppm for 2,4-DNT, which is identified by EPA Hazardous Waste Number D030.

If a facility treats, stores, and/or disposes of hazardous wastes, it must obtain a RCRA treatment, storage, or disposal (TSD) facility permit. All four sites surveyed were either fully permitted or had an interim status permit under RCRA Part B, Subpart X (40 CFR §264.600 et seq.). The primary reason these facilities have applied for and obtained either full or interim status permits is not based on the K045 or K047 wastes, but rather the K044 wastes. Although these explosive sludges are also part of the management of pink water waste they are beyond the scope of this report.

When disposing of listed hazardous wastes, the AAPs must also comply with all applicable land disposal restriction (LDR) requirements. The land disposal of K044, K045, and K047 listed wastes has been effectively banned since August 8, 1988 (40 CFR part 268 et seq.). Pursuant to the regulations, these wastes can be land disposed only if they have first been treated and/or deactivated to remove the reactivity characteristic (see 40 CFR §§268.42 and 268.43).

With regard to the K045 wastes, of the four AAPs surveyed, Crane AAP and Lone Star AAP send all of their spent carbon off-site for recycling or disposal. MAAP sends all of its spent carbon that does not test as reactive off-site for recycling or disposal. It open detonates reactive spent carbon on-site. Kansas AAP treats its spent carbon on-site. The residue and spent carbon determined to be non-hazardous is incinerated in its "contaminated waste processor". To date, no special air permit has been required, but this is subject to change should Kansas revise its air regulations.

2.2.1 Resource Conservation and Recovery Act Reauthorization

Since 1989, Congress has discussed the reauthorization of Resource Conservation and Recovery Act (RCRA). The last time there was a comprehensive reauthorization of RCRA was in 1984, with the Hazardous and Solid Waste Amendments (HSWA). Reauthorization of the CWA, the Superfund legislation (also referred to as CERCLA), and the Safe Drinking Water Act (SDWA) are three examples of legislation currently enjoying higher priority than RCRA reauthorization. Many in Congress expect that it will be at least 1997 before any serious efforts are undertaken to reauthorize RCRA.

EPA is currently working to revise the regulatory definitions of hazardous waste and hazardous waste recycling. These efforts could impact pink water treatment, storage, and/or disposal operations because EPA has stated that, once these changes are in place, the Agency intends to begin emphasizing hazardous waste recycling over treatment and disposal options. A continued increase in the focus on pollution prevention is also expected at EPA.

2.3 Air Regulations

While open burning of spent carbon has been generally discontinued in favor of sending spent carbon off-site for recycling or disposal, air regulations still should be considered. According to the facilities surveyed, most open burning has occurred under special air permits or exemptions obtained from state environmental agencies. For example, MAAP continues to annually renew an open burn and open detonation permit from the State of Tennessee. When spent carbon at MAAP is tested and shown to exhibit the reactivity characteristic, it is open detonated under this open burn and open detonation permit to eliminate the explosives.

2.3.1 Clean Air Act

As various technology alternatives to carbon adsorption are explored, air regulations should be considered in the process. Awareness of applicable air regulations is becoming increasingly important because of their expanding scope and stringency under the Clean Air Act Amendments of 1990 (CAA 1990 Amendments). Areas of major concern for many manufacturing facilities have to do with emissions of volatile organic compounds (VOCs), oxides of nitrogen (NO_x), and hazardous air pollutants (HAPs). Certain pink water treatment activities may be associated with the release of NO_x and HAPs.

The destruction of explosive-laden carbon may involve air emissions containing NO_x. The latter are of concern because these are considered to be precursors of ground level ozone. Ground level ozone has been linked to human respiratory ailments and contributes to visible air pollution, or smog. Ground level ozone is one of several "criteria air pollutants" for which national primary and secondary ambient air quality standards (NAAQS) have been established under Title I of the Clean Air Act, as amended in 1990 (see 42 U.S.C.A. §7409). The current primary and secondary NAAQS for ozone are set at 0.12 ppm. According to the regulations, "the standard is attained when the expected number of days per calendar year with maximum hourly average concentrations above 0.12 ppm is equal to or less than one" (40 CFR §50.9). Therefore, areas will be considered nonattainment if the standard of 0.12 ppm is exceeded more than one day per year.

Since EPA originally established the ozone NAAQS in the 1970s, many areas in the United States have consistently failed to attain the published ambient air quality standards. Congress responded with additional provisions for ozone nonattainment areas in the 1990 Amendments. The goal is for even the most extreme areas of nonattainment to be in compliance with the standards by November 15, 2010. While none of the four AAPs surveyed are currently in an ozone nonattainment area, other plants that do find themselves in nonattainment areas may also find themselves subject to new and more encompassing regulations controlling the emissions of NO_x.

The Congressional listing of 189 HAPs in Title III of the 1990 Amendments includes a mandate that the EPA regulate sources of emissions of the listed HAPs (see generally 42 U.S.C.A. §7412). Major stationary sources of HAPs are defined as sources emitting, or having the potential to emit, 10 tons per year or more of any one HAP or 25 tons per year or more of any combination of HAPs [42 U.S.C.A. §7412(a)(1)]. Area sources, those sources emitting amounts less than the major source threshold, also can be regulated by EPA. Of interest to AAPs is the inclusion of 2,4-DNT on the list of 189 HAPs.

One of the HAP source categories already identified by EPA is the Explosives Production Source Category (see 58 Fed. Reg. 63941, December 3, 1993). National emission standards for hazardous air pollutants (NESHAP) for major stationary sources in the source category are slated for promulgation by November 15, 2000. These standards will be established using the maximum achievable control technology (MACT) for the source category. Currently, there are no plans to regulate area sources in the Explosives Production Source Category. While it is too early to accurately predict, the requirements under this NESHAP may include restrictions on major stationary sources at facilities where the LAP and demilitarization of munitions occur. Ground work to develop this NESHAP is likely to begin in 1996 or 1997.

There are a variety of factors that will decide whether or not an AAP will be subject to regulation as a source of NO_x and/or HAPs. These factors may include: annual emission amounts, facility location, and whether the facility is even emitting regulated air pollutants -- this last factor will depend mainly upon the pink water treatment technology that is employed. For this reason, all federal, state, and local air pollution regulations, such as those discussed above, will be considered in the decision-making process as alternative pink water treatment technologies are evaluated.

3.0 SEPARATION TECHNOLOGIES

Although the thrust of this report is the identification of technologies to destroy toxic nitrobodies in pink water, separation methods were also reviewed. The current two step carbon adsorption process provides reference costs to compare with other separation and destruction processes. Performance production rates, 20 gpm and 200 ppm explosives, are given in Section 1. Sections 5 and 6 provide evaluations of carbon adsorption processes.

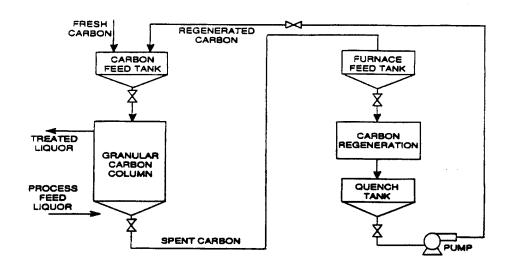
3.1 Granular Activated Carbon Adsorption

3.1.1 Pretreatment and Adsorption

Granular Activated Carbon (GAC) adsorption has the longest history, and is the most mature method used today for the removal of organic materials from wastewater. It is the baseline technology for pink water treatment, capable of reducing effluent nitrobodies to less than 1 ppm. GAC is a non-graphitic, processed form of carbon that contains vast internal porosity, offering a surface area of 300 to 2,500 ft²/lb.9 The GAC is packed into columns through which the liquid to be treated is passed. Pink water is pre-filtered, using 10 micron paper, prior to GAC treatment in order to remove sediment formed during settling that would otherwise reduce the adsorptive capacity of the GAC. Contaminants are adsorbed on the GAC surfaces as the explosives-contaminated water flows through the column. Contaminant loading on the carbon is commonly 30% for pink water treatment. After the carbon is loaded with contaminants, it must undergo another treatment process. Specifically, the adsorbed toxic compounds must be converted into innocuous degradation products such as N₂, H₂O, and CO₂. Figure 3-1 shows a typical GAC process as used in most industries.

In addition to several GAC treatment technology options, there is significant variability in the composition of pink water from different sources. As in any process waste stream, pink water can include dissolved and colloidal metals, salts, metal fragments, oils, greases, and plasticizers. In addition, other variables influence treatment effectiveness and costs such as treatment facility size (i.e. capital cost), plant throughput, frequency of operation, loading rates, waste water temperature, and pH.

Figure 3-1
Typical Granular Activated Carbon Process with On-Site Regeneration



Capital and operating cost estimates for GAC treatment, followed by either off-site thermal regeneration or incineration, are given in Section 5. These costs are based on a 1992 survey of AAPs. These recent data provide an important reference for economic comparison.

3.1.2 Thermal Regeneration and Incineration

Thermal regeneration, the most common method of reactivating contaminated GAC, has had varying success at Department of Defense (DOD) facilities. Although nitrobodies are destroyed during regeneration, the regenerated GAC has impaired performance. For example, several carbon regeneration technologies yield a carbon product that suffers from attrition (due to fragmentation, formation of fines) and loss of adsorptive capacity. GAC losses during regeneration are significant, amounting to as much as 50%.

Typically, regeneration occurs at temperatures in the range of 1,600° to 1,800°F with a carbon residence time of 30 minutes. Air pollution control equipment, such as afterburners and particle removal systems, is required. Descriptions of three regeneration systems (fluidized bed, rotary calciner, and multiple hearth furnace) are given below.

A fluidized bed furnace is a cylindrical structure with a refractory lined shell containing a bed of hot, abrasive media, usually silica sand. Air is passed upward through the media at speeds of 1.5 to 3 feet per second, causing the sand to expand 40% to 60% in volume and churn in a fluid-

like manner.¹² The light churning abrasive action of the fluidized media removes contaminants from the GAC surface and the organic constituents are destroyed due to the extreme heat. Fluidized bed techniques have been successfully demonstrated for both the destruction and regeneration of explosive-laden GAC.^{13,14} However, regeneration of GAC using fluidized bed technology results in large attrition losses, about 15% to 20%. In addition, the adsorptive capacity of regenerated GAC is about 65% to 72% of the virgin carbon. Thus, about 50% of the GAC function is lost.

The rotary calciner, a heated, rotating tube treated explosive-laden GAC at the Iowa AAP.¹³ Explosive-laden carbon was introduced at the higher end of the tube, which was nearly horizontal. The carbon gradually tumbled to the lower end of the tube as contaminants were thermally destroyed. Carbon collecting at the bottom of the tube was easily recovered.

The multiple hearth furnace is a wide, vertical tube containing a number of circular shelves. ¹⁵ Carbon is introduced through the top of the furnace onto the top shelf. Arms attached to an axial rotary shaft gradually rake the carbon off the shelf causing the carbon to fall to the second shelf. A continuous series of rakings and fallings to each successive lower shelf proceeds until the carbon falls to the bottom of the furnace. The ash or residue that remains is removed from the bottom of the furnace. The cost data, used in later analyses, were obtained from recent literature pertaining to off-site incineration. ¹⁶

3.2 Resin Adsorption

Polymeric resin adsorption has been evaluated and laboratory tested for pink water treatment. However, resins can be regenerated less expensively than activated carbon.¹⁷ Several resin beads have been evaluated as replacements for GAC.¹⁸ Resin beads, consisting of a styrene and divinyl benzene copolymer, are easy to regenerate through numerous cycles. Ion exchange resins, on the other hand, are not very effective for treating pink water because explosive compounds are large molecules and non-ionic. Furthermore, ion exchange resins offer only about 14% of the adsorptive capacity of activated carbon.⁴

Resin adsorption has never been implemented as an alternative to activated carbon for pink water treatment. Thus, bench-scale and laboratory testing must be performed in order to determine costs associated with the process. However, capital and operating costs for polymeric resin adsorption systems vary due to the

The economic estimation does not specify off-site furnace type. Incineration costs are based on what a vendor charges to transport and incinerate spent carbon.

same factors that cause GAC cost to vary. If theoretical resin adsorption facility costs are compared with GAC, the resin process is more expensive than GAC with thermal regeneration.¹⁸

As with GAC, the resin adsorption technique merely removes contaminants from the waste water stream, and captures them on resin particles. Resin adsorption does not destroy the contaminant. A secondary process such as solvent extraction must be used to remove the contaminant from the resin without destroying the resin beads. Typically, acetone and toluene have been used in the solvent extraction process. However, the extracted material has not been destroyed and still presents disposal concerns. Also, the use of organic solvents may introduce problems with VOCs and HAPs due to solvent venting to the atmosphere.

3.3 Surfactant Complexing

Surfactant treatment of ammunition plant waste water on a laboratory scale has shown that both TNT and RDX can be removed from solution in about one hour. The optimum conditions for treatment appear to be a combination of pH 11 and 0.4 mole of a quaternary surfactant (N,N,N¹, N¹,N¹-pentamethyl N-tallow 1,3 propane diammonium chloride) for each mole of TNT in solution.

Although the cost of chemicals is quite low, Ciccone reports total process costs are about twice the cost of GAC adsorption with thermal regeneration. ¹⁹ In addition, work needs to be completed pertaining to effluent analysis and neutralization of the filtrate. This work is required prior to discharge, in order to insure compliance with NPDES limits.

As with other separation techniques, surfactant complexing only removes the pink water pollutants from solution and creates a solid waste. A second treatment is required to destroy the complex nitrobodies. Secondary treatment was not included in the above cost data.

3.4 Liquid-Liquid Extraction

Liquid-liquid, counter-current extraction is a method of transferring a solute from one solvent stream to another by mixing an extracting solvent with a solution that requires extraction. The extracting solvent must be immiscible in water and possess a high affinity to the water contaminants. A liquid-liquid extraction system for treating pink water consists of an extraction column, a continuous distillation column, and a steam stripping column.

Brown and Jackson, working at Picatinny Arsenal, NJ, described such a twophase system for removing nitrobodies from pink water streams using synthetic white oil (ISOPAR H) on a laboratory scale.²⁰ Economic estimates associated with white oil extraction techniques range from about half the cost of carbon treatment with thermal regeneration to equal that of carbon treatment without regeneration. However, photochemically reactive nitrobodies in the waste stream were not extracted by the white oil.

Tash, Layne, and Goodfellow, using toluene as the extractant in laboratory scale experimentation, obtained a reduction of TNT concentration to below 1 ppm. ²¹ The solubility of RDX and HMX in toluene could not be located. Using the Tash, Layne, and Goodfellow work as his source of data, Ciccone scaled the process cost estimates to 100,000 gallons per day. ^{19,21} His data projected the liquid-liquid extraction costs to be \$40-\$50/1,000 gallons on a continuous basis. At lower production rates, treatment costs would be even higher. According to recent vendor information, capital costs for treating 20 gpm of pink water would be approximately \$900,000. ²² Bench-scale testing is needed in order to obtain accurate operating costs

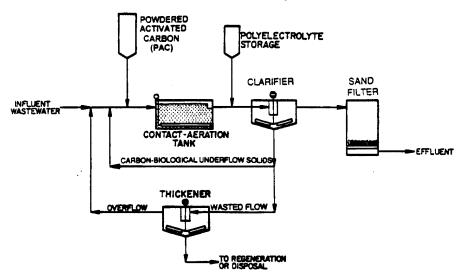
In liquid-liquid applications, the contaminant is not destroyed, but is only transferred from a water stream to the extracting stream, which then must undergo further processing. In Ciccone's estimates, the explosive-toluene stream is distilled; the toluene is recycled and a concentrated explosive sludge is incinerated. Cost estimates did not include the incineration step.¹⁹

3.5 Powdered Activated Carbon Systems

Powdered activated carbon (PAC) systems generate a slurry by treating a liquid stream with PAC in a tank. The treated stream and spent carbon exit to a second tank followed by filtration or settling. PAC systems equalize the concentration of impurity adsorbed and impurity remaining in the liquid. After reaching equilibrium, additional PAC is added to remove more contaminant. Full-scale PAC systems have not been used to treat pink water; thus, full-scale treatment costs are unavailable. Bench scale and further laboratory testing are needed to collect data for process and cost calculations.

PAC is about two-thirds the cost of GAC, and is used in many water and waste water treatment plants to remove unwanted organic constituents from liquid streams. However, PAC requires more maintenance than GAC, dosage measurements need to be taken, and separation from treated solution is required. Pilot plant experiments involving Atomized Suspension Technique (AST) regeneration of powdered carbon have been described by Buckley, Jackson, and Roth and by Leeper, et al. 23,24

Figure 3-2
Typical Process Flow Diagram of a Powdered
Activated Carbon System



In AST, a slurry of spent powdered carbon in water is atomized into a heated, oxygen-free, vertical tube. The water quickly vaporizes, and the carbon is heated to over 1,200°F. The explosives are destroyed, and the hot carbon drops through the column and is reactivated.

Because of high costs associated with continuous dosing and separation of carbon from slurry, PAC compares unfavorably with other technologies for pink water treatment. Vendors do not recommend use of PAC over GAC. In fact, overall PAC is more expensive, more time consuming, and requires more area to operate than GAC, while offering the same treatment results.²⁵

3.6 Ultrafiltration

Ultrafiltration is usually used to remove either suspended solids or very large molecules from aqueous waste streams.²⁶ A membrane retains solids and molecules with molecular weights over 1,000, while water and smaller molecules pass through. Membranes in the form of hollow-fiber modules, are connected in series, providing maximum membrane area with minimum space and reasonable flow and pressure requirements.²⁷ However, TNT has a molecular weight of 227, too low for effective ultrafiltration.

Nevertheless, Ciccone made certain assumptions using an ultrafiltration technique for pink water treatment for comparison. Costs were 35 times more expensive than GAC, making it the most expensive method investigated in his report.¹⁹

3.7 Reverse Osmosis

Reverse osmosis (RO) is a membrane separation technology suggested to treat pink water. RO has been used successfully in industry to purify water, and to concentrate dilute salt solutions, usually compounds with MWs less than 300. The principle of operation is based on osmosis, a naturally occurring process in which a fluid flows across a semi-permeable membrane. The driving force behind this phenomena is the chemical potential difference between the fluids on each side of the membrane. Semi-permeable membranes, in theory, allow pure water to flow through them while rejecting dissolved solids from passage. RO is achieved by applying pressure to drive the separation in the opposite direction to naturally occurring osmosis. Thus, high pressure pushes pure water through the membrane.

RO separates pink water into a permeate stream containing less than 1 ppm explosives, and a retentate stream concentrating the nitrobodies. RO is a water separation process which produces a pure water stream. The process also produces a slightly concentrated contaminant stream requiring further treatment. This concentrated stream amounts to approximately 85% of the original pink water stream. Thus, organic solids concentration increases by only about 15%, a marginal improvement. The estimated separation costs to achieve this small concentration change are approximately \$5/1,000 gallons feed.²⁸ Pink water processing by RO is not cost effective.

3.8 Other Technologies Considered

The following separation technologies were considered and reviewed:

- 1. Distillation
- 2. Foam separation
- 3. Liquid membrane separation
- 4. Settling with further treatment.

All of these, however, were eliminated because of technical and cost issues. Technical issues include required long processing time and contaminant removal efficiency. Therefore, because of technical difficulties, operating and capital costs would be considerably high.

4.0 DESTRUCTION TECHNOLOGIES

This section contains technology descriptions, including a graphic, where appropriate, comparing the candidate process to the currently used GAC process. However, detailed discussions of the selection and evaluation process are reserved for Section 5 and Section 6. Assumed operating conditions for these processes are a pink water flow rate of 20 gallons per minute (gpm) and a total explosives concentration of 200 ppm.

As a goal, destruction technologies described here convert the toxic constituents of pink water to innocuous products such as N_2 , O_2 , H_2O , and CO_2 . The extent to which this goal is achieved is a vital issue that must be resolved with certainty. Both regulated concentrations and toxicity of the effluent must be measured as part of technology qualification. After processing, the treated waste stream must meet proposed discharge limits, and must not contain contaminants posing a future regulatory problem.

The more than 25 technologies evaluated can be classified into seven groupings:

- 1. Base-catalyzed hydrolysis,
- 2. Advanced oxidation processing (AOP) [e.g. ultraviolet oxidation with hydrogen peroxide (H₂O₂)],
- Electrolytic processing,
- 4. Hydrothermal and thermal processing [wet air oxidation (WAO), supercritical water oxidation (SCWO), NitRem process, and Plasma Arc Technology (PAT)],
- 5. Electron beam processing,
- 6. Biological, and
- 7. Combinations of the above.

These technologies are compared with the currently used GAC processes involving both thermal regeneration and incineration as a reference.

4.1 Base-Catalyzed Hydrolysis

Base-catalyzed hydrolysis is an effective method for decomposing nitro-organic compounds. ^{29,30,31,32,33,34} Water solutions and slurries of the nitro-organic compounds are mixed with a two- to three-fold excess of sodium hydroxide (NaOH). As the mixture is heated, usually to temperatures just below 212°F, the solutions develop a range of colors (from light yellow to deep reds and browns, depending on the starting material and concentration). The color changes indicate dissolution and reaction between the nitro-organic compounds and the NaOH.

Typical hydrolysis products for a triple-base propellant M31A1E1 are formate, oxylate, cyanate, urea, propionate and inorganic carbon as CO₃⁼ and HCO₃⁻, with a total of about 8,624 ppm carbon. This hydrolyzed solution is then diluted to

about 1,000 ppm carbon and processed further in supercritical water, using hydrogen peroxide as the oxidizer for the carbon. In the case of the M31A1E1 propellant, the combined hydrolysis/SCWO treatment resulted in complete oxidation of the organic carbon below 0.1-ppm detection limits. Total inorganic carbon was about 325 ppm. Researchers also recorded that 64% of the nitrogen is lost in the hydrolysis step via formation of gaseous N₂O. The nitrogen remaining in solution is primarily associated with urea, nitrite, and nitrate. Urea is converted to NH₃ and then to N₂. Residual NH₃ is destroyed to below 0.03-ppm NH₃ detection limits in the SCWO process. However the destruction of nitrate is incomplete, with the degree of destruction depending on oxidizer concentration.

Toxicity testing data of the effluent stream were not reported, and cost data were not presented for the combined hydrolysis/SCWO process. In a recent presentation, the same researchers reported on base-catalyzed hydrolysis followed by either biotreatment or SCWO, but again gave no specific data on effluent toxicity or composition.³⁷

Base-catalyzed hydrolysis is not considered to be a viable treatment technology for pink water and explosive-laden GAC, even though specific data were unavailable. This technology is too complex, energy intensive, and costly. Because the technology was in the early stages of development, commercial test equipment is not available.

4.2 Advanced Oxidation Processes

4.2.1 Background

There are a number of advanced oxidation processes (AOPs) being investigated for treating aqueous waste streams. Several of these are described below.

Ultraviolet (UV) light in combination with 10 to 200 ppm hydrogen peroxide (H₂O₂) effectively cleared aqueous solutions of 2,4,6-C-labeled TNT by conversion to CO₂. Aqueous solutions of RDX, HMX, 2,4-DNT, 2,6-DNT, Explosive D (ammonium picrate), and pink water also were treated. AOP technologies are developing rapidly. Work is continuing to evaluate catalysts such as TiO₂ and UV pretreatment prior to biological treatment of wastewater.

The advanced oxidation process forms highly reactive, powerful, nonspecific, oxidizing hydroxyl radicals (*OH) in solution. Dissolved organics are oxidized by *OH to H₂O, CO₂, and dilute mineral acids. The

hydroxyl radical extracts hydrogen atoms from stable compounds, thus beginning a decomposition chain reaction. 41,42,43

Several problems are associated with UV treatment of pink water streams. TNT produces more stable compounds, 1,3,5-trinitrobenzene (TNB) and breakdown products, requiring longer treatment times. Additionally, UV light penetrates only a relatively thin layer of nitrobody-colored water, and often the stream must be diluted to minimize UV light attenuation. AOPs are usually only cost effective down to 1 ppm. Also, wax and microbial growth in the waste stream can coat the quartz tubes, separating the lamps from the waste streams, and attenuate the UV light. The coating problem has been addressed by one supplier, who has a patented wiper system to clean the quartz tube. To Some AOPs use ozone, leading to ground level ozone concerns; these problems may be avoided with properly installed ozone production and treatment systems.

To overcome the problem of dissolved metals in pink water waste streams, Milan AAP used electrochemical precipitation. MAAP also found that $UV-H_2O_2$ does not improve the destruction rate or efficiency for explosives over using UV only. Optimal destruction rates require pH adjustment to make pink water slightly basic. Most pink water contaminants were completely destroyed with a retention time of 80 minutes, however TNB was not destroyed even after 200 minutes.⁴⁴

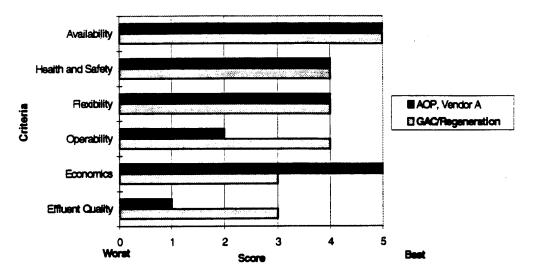
AAPs have treated pink water and RDX with some success at the pilot-scale; reducing the level of TNT to under 1 ppm. Building on these results, work has continued to exploit AOPs on waste streams, and several companies are currently manufacturing commercially available UV-ozone or UV-H₂O₂ systems. Low pressure UV lamps work best with oxidation processes using H2O2 and ozone. However, in catalytic AOPs, such as titanium dioxide, medium pressure lamps perform best. 2

4.2.2 Advanced Oxidation Process, Vendor A

This system purifies water by removing a host of pollutants, including TNT and propellant compounds. ^{47,53,54} H₂O₂ is the source of *OH radicals. Transportability is a significant advantage of this technology and equipment can be taken for evaluation to facilities generating pink water. ⁵³ Capital costs were estimated by the vendor at \$185,000 for a 20 gpm plant and \$250,000 for a 200 gpm plant. ^{55,56} Although the vendor claims complete destruction of explosives with its process, other studies, including one at MAAP, indicate that H₂O₂ without UV is ineffective. Also, the process appears to be significantly more costly than GAC.

The AOP-Vendor-A technology is compared with the reference GAC process in Bar Chart 4-1. As can be seen, the advanced oxidation process scores higher than GAC only in the economics criterion. AOP scores lower in key performance criteria such as operability and effluent quality. Indeed, evidence suggests this process may not work for pink water.

Ber Chart 4-1
Criteria Comparison Between AOP, Vendor A and GAC Followed by Regeneration

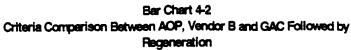


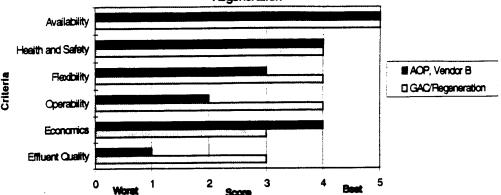
4.2.3 Advanced Oxidation Process, Vendor B

Another vendor of AOP systems capable of treating explosives-contaminated waste water recently supplied units to MAAP and to the Naval Surface Warfare Center at Indian Head, Maryland. ^{57,58,59} The unit at MAAP has demonstrated technical and operational abilities in treating TNT and RDX contaminated groundwater. However, carbon adsorption of trinitrobenzene is required. Work at the Indian Head is directed toward the treatment of waste water containing nitrate esters. ⁵⁷ Based on the vendor's informal estimates, capital equipment costs are about \$492,000, depending on oxidant requirement. ^{57,60}

The AOP-Vendor-B technology is compared with the reference GAC process in Bar Chart 4-2. As can be seen, the advanced oxidation process scores higher than GAC only in the economics criterion. This AOP scores lower in operability, effluent quality, and flexibility. Indeed, evidence suggests this process may not work for pink water.

Evaluation methods and results are detailed in Section 5 and Section 6.





4.2.4 Fenton's Chemistry

Fenton's Chemistry uses H_2O_2 and ferrous sulfate, in a batch reactor. The process chemistry dates back to 1804 when H.J.H Fenton reported that the ferrous ion promoted the oxidation of malic acid by hydrogen peroxide. In the 1930s, the reaction mechanism was detailed, and the hydroxyl radical was identified as the reactive species.⁶¹ Hydroxyl radicals are generated in acidic, aqueous solution by the following reaction:

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^- + OH^-$$

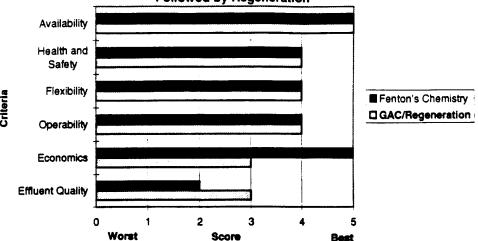
Fenton's Chemistry occurs optimally at a final pH of 3 or 4. The treated waste stream must be neutralized by caustic addition prior to discharge. Fe(OH)₃ precipitates out of solution, but can easily be recovered in a settling tank or a centrifuge. This iron sludge usually can be used again as the reaction catalyst, after re-acidification. This process has shown significant results in the destruction of organic acids, alcohols, aldehydes, amines, aromatics, and photochemical wastes.⁶² Retention times for 95% contaminant reduction are typically 30 to 60 minutes.

This process is commercially available, fully automated, and skid-mounted. These characteristics allow for easy operation and increased portability. Estimated capital costs are just over \$200,000.⁶³

The Fenton's chemistry technology is compared with the reference GAC process in Bar Chart 4-3. As can be seen, Fenton's chemistry process scores higher than GAC only in economics. Fenton's process scores lower in the important effluent-quality criterion.

^{*} Evaluation methods and results are detailed in Section 5 and Section 6.

Bar Chart 4-3
Criteria Comparison Between Fenton's Chemistry and GAC
Followed by Regeneration



4.2.5 Other Oxidation Processes

Two additional AOPs are Oxone[®] and a titanium dioxide based process. These processes work like the other AOPs, but use a catalyst to produce the hydroxyl radical.

Oxone®

Another oxidizing agent, a mono-persulfate mixture, Oxone has been used with H_2O_2 in some experimental work. However, it was not as cost effective as the other processes because Oxone is more expensive than peroxide.

Titanium dioxide

Titanium dioxide (TiO₂) is a photocatalyst, activated when exposed to light from the near UV portion of the spectrum, 300-390 nm. As the TiO₂ absorbs a photon, an electron is promoted from the valence band into the conduction band, leaving behind an electron hole. This electron hole oxidizes water to a °OH. TiO₂ powder can be mixed with pink water and pumped through solar reactors. After reaction, the water-photocatalyst slurry is filtered and the TiO₂ is recycled through the system.⁶⁴

Prairie, et al. performed experiments on simulated pink water using TiO₂. ⁴⁰ The simulated pink water contained either 90 ppm TNT or 48 ppm RDX dissolved in deionized water. Batch runs were performed in a jacketed glass reactor vessel. Anaerobic and aerobic experiments were conducted. Under aerobic conditions, the intermediates formed leveled off at 15 ppm after 220 minutes. However, under anaerobic conditions, intermediates

^{*}Oxone* - E.I. DuPont Nemours, Inc., a mixture of potassium mono-persulfide, potassium sulfate and potassium hydrogen sulfate.

were not formed. The anaerobic process results in slightly slower reaction times, but produces much lower levels of reaction by-products. RDX reactions were much faster than TNT reactions, while no intermediates were formed. Prairie, et al. concluded that anaerobic photocatalysis appears to be attractive for treating TNT and RDX. Also, since biodegradation of TNT is possible, they suggest photocatalytic degradation followed by a conventional biological treatment.

Although cost data were not presented, the TiO₂ catalyzed process should be as expensive as other AOPs. TiO₂ experimental work on pink water suggests this process is not a viable treatment process since it does not effectively treat TNT.

4.2.6 Summary

Both H₂O₂ and O₃ are effective oxidants, but H₂O₂ appears to be the more practical choice. It is more economical, and easily purchased, diluted, and introduced into the reaction vessel.⁴² Ozone must be generated by a relatively expensive, energy-intensive system, which increases processing cost. Additionally, O₃ systems may require a destruction system to destroy any residual ozone before being released. Ozone systems have been shown to be more cost effective than straight UV-H₂O₂ processes in certain applications.⁴³ All of the AOPs have relatively low total treatment costs, and have mobility and flexibility features unavailable from most other destruction processes. Catalytic AOPs are probably only cost effective down to a to-be-determined concentration. As a result, a follow-on processing step, e.g., GAC, will be required. A cost benefit determination of such a system requires bench-scale testing.

4.3 Electrolytic Processing

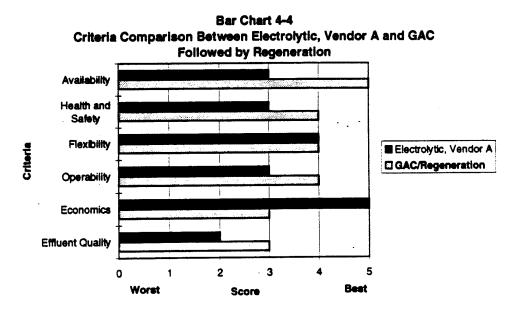
4.3.1 Electrolytic Process, Vendor A

A patented electrolytic cell and process for generating a mixed-oxidant solution from a 10- to 30-wt.-percent salt brine was described by its technology owner. The flow-through electrolytic cell, operating at 6 to 12 volts, generates a mixed-oxidant solution containing 200- to 300-ppm chlorine, 40- to 60-ppm chlorine dioxide, and 10- to 20-ppm ozone. The inventors consider their technology proprietary, and claim that these components react with contaminants in solution and decompose or deactivate by an oxidation mechanism. However, published data are sparse.

When effluent from the electrolytic cell was added to a test solution of deionized water containing toluene, ethyl benzene, and xylene, the organics were destroyed to levels below detection limits, i.e., <5 ppm. ⁵⁷ Trichloroethane treatments yielded destruction levels down to 5 ppb. Although targeted compounds are destroyed, the identity of products produced is required to establish validity. The process primarily produces potable water from contaminated groundwater, but considering results obtained, the process may have merit for pink water. Questions about the formation of halogenated organics during treatment have been raised. The inventors, basing their judgment on previous testing of waste waters, seriously doubt that any halogenated organics will form while treating pink water. ^{67,68,69}

Work is continuing, but the process, as it relates to pink water treatment, is at an early stage of technical maturity. The vendor is attempting to obtain support to continue exploratory efforts. Small, compact, and portable equipment is available to use for testing a 20 gpm waste stream. Capital costs were estimated to be around \$100,000.⁶⁷ This is one of the least expensive destruction processes.

The Electrolytic-Vendor-A technology is compared with the reference GAC process in Bar Chart 4-4. As can be seen, the Electrolytic-Vendor-A process scores lower than GAC in all the performance criteria, except for economics.



Evaluation methods and results are detailed in Section 5 and Section 6.

4.3.2 Electrolytic Process, Vendor B

Another electrolytic technology destroying nitrobodies in TNT-contaminated waste water claims to produce non-toxic effluents. A three-phase study involved: 1) laboratory work on 100 mg quantities of TNT waste-water components (e.g. sulfonated isomers of TNT), 2) analytical techniques to determine the composition of the waste water as a function of electrolysis reaction time, and 3) a bench-scale demonstration system.

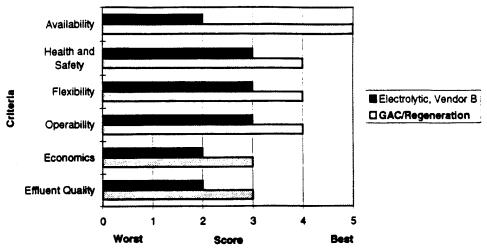
In laboratory studies, TNT was reduced at the cathode to about 1 ppm in a sodium salt solution (similar to the inorganic salt concentration of the TNT waste water). The electrolysis reaction established conditions for intense electrochemical oxidation, as well as reduction at the opposing electrode surfaces. Results of scaled-up experiments were mixed. That is, target compounds were destroyed sometimes, but degradation was not observed in other experiments. In the cases where destruction was successful, the required residence time in the electrolytic cell was of the order of 24 hours. Although this technique shows promise, considerable effort is needed to develop the technology. Many questions are unanswered; for example, data reproducibility, products formed, effluent toxicity, and cost.

Recently, preliminary tests on "simulated" pink water, consisting of TNT and RDX, yielded favorable results. Reaction times of just over one hour achieved RDX concentrations below 20 ppm and TNT concentrations below 0.3 ppm. Questions concerning the formation of triaminotoluene were not addressed; further study is required. Estimates of operating costs show utility usage is a major cost. Predicted capital costs were a little over \$300,000. The scale-up factor is over 6,000 to 1, and this large ratio introduces uncertainty in the results. As the process approaches technical maturity, savings from process optimization should occur. However, at this time, this process does not seem economically feasible for pink water treatment.

The Electrolytic-Vendor-B technology is compared with the reference GAC process in Bar Chart 4-5. As can be seen, the Electrolytic-Vendor-B process scores lower than GAC in all the performance criteria.

^{*} Evaluation methods and results are detailed in Section 5 and Section 6.

Bar Chart 4-5
Criteria Comparison Between Electrolytic, Vendor B and GAC
Followed by Regeneration



4.4 Hydrothermal and Thermal Processing

4.4.1 Background

The term hydrothermal processing, in the present context, includes three different technologies, each with its own set of operating parameters. These processes are: wet air oxidation (WAO), supercritical water oxidation (SCWO), and the nitrogen removal process (NitRem). NitRem is a high-temperature, high-pressure process using both oxidation and reduction chemistries and a patented reaction vessel. The only thermal process considered is plasma are technology (PAT). These technologies are grouped together because of similar concept and process economics. As a result of the large energy input required to heat water in dilute waste streams, these technologies are costly. Consequently, hydrothermal and thermal technologies are not cost-competitive with other treatments for dilute aqueous streams. In the interest of completeness, however, related work is discussed below.

4.4.2 Wet Air Oxidation

Considerable work on WAO was performed by Phull at the University of Maryland, and the U.S. Army Construction Engineering Research Laboratory, Champaign, Illinois. Total organic carbon (TOC), initially about 1,300 mg/l, and chemical oxygen demand (COD), initially around 2,000 mg, were reduced by almost 100% at reaction temperatures of 390° to 645°F, and pressures of 2,150 psi. Although directed toward red water research, this technology could be applied to pink water streams, but at

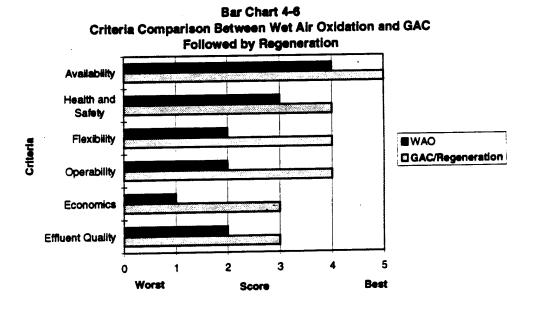
very high cost. Additional work evaluated catalysts for WAO processes and feedstocks. 75,76

The waste stream from red water treated by WAO was shown to be more toxic than the starting material.⁷³ However, the composition and chemical structure of the resulting toxic mixture was not reported. Maloney, et al. suggested conventional biological treatment following WAO to significantly reduce toxicity of the effluent stream.⁷⁴

At least one research group used WAO on propellants^{77,78} and propellant waste water streams containing torpedo-propellant, OTTO Fuel, and hydrazine-based rocket fuels. Temperatures used were in the range of 404° to 410°F, reactor pressure was 800 psig, and the flow rate was 5 gpm of the water-propellant slurry. However, data for effluent toxicity and cost were not presented.

An example of commercial success in this area is the delivery of multiple WAO units to the Taiwanese Petroleum Corporation to treat spent caustic liquor from ethylene production.⁷⁹ However, for pink water applications, this process is too energy intensive and too expensive. A vendor estimates capital costs reaching \$3 million.^{80,81} Concentrating the pink water would lead to lower treatment costs but the vendor could not give any specific estimate.

A WAO process with GAC polishing is compared with the reference GAC process in Bar Chart 4-6. As can be seen, the WAO-GAC process scores lower than GAC in all the performance criteria.



^{*} Evaluation methods and results are detailed in Section 5 and Section 6.

4.4.3 Supercritical Water Oxidation

Supercritical water oxidation (SCWO) is a hydrothermal process that operates above the 705°F critical temperature of water. The critical point pressure is 22 bar, i.e., 3,500 psi. Near the critical point, the solubility of an organic compound in water correlates strongly with density; therefore, solubility is very pressure dependent in this region. For example, the solubility of benzene in water at 77°F is only 0.07 wt %, but at 500°F, the solubility is about 7 to 8 wt %, and relatively independent of pressure. At 549°F, the solubility is somewhat pressure dependent with a maximum of 18 wt % at 20 to 25 bar. In this pressure range, the solubility rises to 35 wt % at 560°F, and at 572°F the critical point of the benzene-water mixture is surpassed. When the mixture becomes supercritical, by definition, there is only one single phase and the components are soluble in all proportions.⁸²

In contrast to the high solubility of organics, the solubility of inorganic salts in supercritical water is low. For example, the solubility of NaCl is about 37 wt % at 572°F and only about 120 ppm at 1,020°F and 25 bar. This large difference in solubility allows the separation of salts from supercritical reactors.

When SCWO is applied to energetics, the reactor is typically fed by three separate streams. Frequently, the waste and caustic streams are mixed together prior to injection in the reactor, then compressed to about 25 atmospheres and essentially pre-reacted. The third feed stream, air or oxygen, is fed separately to the reactor. The organics oxidize at the high temperatures and pressures, and the heat of reaction raises the temperature to between 1,020° and 1,200°F. Acids formed by reaction of halogens in the waste are neutralized by the caustic in the feed, forming inorganic salts. The salts precipitate during pressurization and are removed through the bottom of the reactor. Oxidized products leave through the top of the reactor where they are cooled, scrubbed, and vented. In some cases a polishing step may be used to remove metals from the water e.g., with ion exchange or precipitation processes.

An interesting approach to conducting high-pressure and high-temperature reactions has been deep well injection using the hydrostatic head of the fluid in the well bore to provide the necessary pressure level. Positive features of the SCWO process are high levels of destruction of diverse waste streams. The major drawbacks are the high pressure required and corrosion of the reaction vessel. 84,85

Although cost estimates are speculative, the inventor of the SCWO process suggests that at 570°F, 10% slurries of energetic-contaminated water can be treated at the rate of 300 lb of energetic material per hour, for an operating cost of about \$700/ton. If pink water is first treated with GAC, followed by a SCWO treatment of slurried, explosive-laden carbon, treatment costs are under \$60/1,000 gallons, requiring only \$700,000 for purchased equipment. This cost reduction is due to lower flow rates and fuel oil requirements. Although no direct cost comparisons with WAO or SCWO were given, the author concluded that SCWO should be 20% to 25% less expensive, because it avoids a step requiring compression of air or oxygen prior to injection into the process. Although not specifically addressed, concentrating the pink water (by means other than GAC) could reduce operating costs minimally.

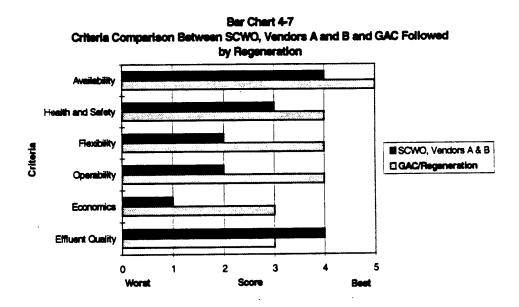
The potential for SCWO to provide an economically competitive control technology for selected hazardous wastes is very high. Bench- and pilot-scale SCWO tests have yielded positive results in terms of high destruction efficiency, lack of NO_x formation, and successful salt removal. The resolution of process development issues, related to scale-up and long-term, reliable operation, remain. ⁸²

SCWO is under investigation by at least four different groups, three private companies, and Los Alamos National Laboratory. One vendor is the leader in the above-ground SCWO research effort, with numerous patents and over eleven years of experience in the development and application area. Most groups are targeting large volume, hard to destroy waste streams such as energetics, industrial waste waters, and sludges.

Although economic predictions for SCWO have appeared in the literature, there is uncertainty with scale-up from pilot- to commercial-sized systems. Therefore, cost estimates are viewed with reservations. One vendor has predicted SCWO capital expenditures in excess of \$2 million for a 20 gpm process. Another vendor predicts similar cost figures. Since energetic contaminants in pink water do not add significant exothermic reaction heat, energy input requirements result in high cost.

SCWO has shown greater than 99.99% destruction efficiency without dioxin formation in the destruction of PCB and DDT. Similar or higher destruction limits have been shown for pharmaceutical and biopharmaceutical wastes, total organic carbon, and thermophilic bacteria. However, scale-up data from laboratory- and pilot-scale to commercial-size systems are not readily available. Additionally, a vendor suggests a 24 hour/day operation of SCWO processes, taking away from process flexibility. As with WAO, SCWO is too energy intensive and too expensive for pink water treatment.

The SCWO technology for both Vendors A and B is compared with the reference GAC process in Bar Chart 4-7. As can be seen, the SCWO process scores lower than GAC in all the performance criteria, except effluent quality.



^{*} Evaluation methods and results are detailed in Section 5 and Section 6.

The GAC-SCWO technology is compared with the reference GAC process in Bar Chart 4-8. As can be seen, the GAC-SCWO process scores lower than GAC in all the performance criteria, except effluent quality.

Followed by Regeneration

Availability
Health and Safety
Flexibility
Operability
Economics

Effluent Quality

Bar Chart 4-8
Criteria Comparison Between GAC Followed by SCWO and GAC
Followed by Regeneration

4.4.4 Nitrogen Removal (NitRem) Process

The NitRem (<u>nitrogen removal</u>) process is a non-catalytic, hydrothermal process that converts aqueous nitrogen compounds such as nitrates, ammonia, and amines into their elemental components. The process patent is held by Battelle's Pacific Northwest Laboratories. The NitRem process accomplishes this chemistry in the condensed, aqueous liquid phase at temperatures of 660° to 715°F and pressures of 2,500 to 4,500 psi. There are two variants of the process chemistry. Key variables are pH and the oxidation state of the nitrogen; for example, whether nitrate or ammonia.

If the waste stream contains oxidized nitrogen compounds, nitrates and nitrites can be destroyed by the addition of formic acid, a formate salt, ammonia, or an ammonium salt. Nitrates and nitrites react with formate ions over a wide pH range (pH 4 to pH 13), and with ammonium ions in an acidic to neutral range (pH 2 to pH 7). This nitrogen oxidation-reduction chemistry permits removal of nitrogen compounds down to a few parts per million. The previously discussed WAO and SCWO technologies treat the carbonaceous fraction of waste waters and leave ammonia in the effluent liquid. NitRem destroys the ammonia by the addition of nitrates and reduces the ammonia load to wastewater treatment plants.

^{*} Evaluation methods and results are detailed in Section 5 and Section 6.

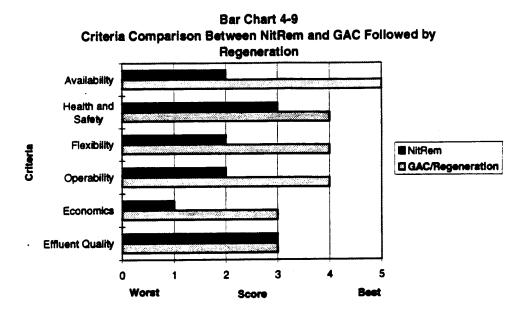
Applications claimed for the NitRem process are ammonia-containing waste waters, nitrates, and energetic waste waters. 98 Other waste streams such as dves and pyrotechnics may be suitable candidates for destruction using the NitRem process. However, the technology has not been demonstrated beyond laboratory scale, and the high cost will likely severely restrict its use. In addition to the patented chemistry, the NitRem process uses a uniquely designed and patented dual-shell, pressure balanced reaction vessel. 99 The pressure vessel itself is constructed of carbon steel and stainless steel components, such as heavy pipe and standard fittings. A removable titanium insert fills the inner part of the pressure vessel where the reaction is conducted. A pressure transfer fluid is placed in the annulus between the steel pressure vessel and the specialty metal reactor vessel. The pressure outside and inside the reaction vessel is constant, and a thin wall of 0.040 to 0.060 inch thick is adequate. Since it is not a pressure vessel, the cost of the specialty metal working reactor is modest and the reactor vessel insert can be replaced rather than replacing the more expensive pressure vessel. Many of the high-pressure and high temperature processes such as SCWO are extremely corrosive, and even the specialty metal working reactor may need to be replaced frequently for continuous use applications. The built-in removal and replacement features mean less down time and relatively easy recovery and recycle of expended inserts made of high value metal alloys.

Another design feature of the dual shell, pressure balanced reactor is the inclusion of a built-in scraper device to provide mixing and cleaning of the reactor vessel surface. This reactor-scraper combination appears to offer safety features not inherent in standard, lined pressure vessels. For example, in severe corrosive environments, lined pressure vessels face the potential safety hazard of liner leaks and hidden corrosion of the pressure vessel. This hidden corrosion can lead to catastrophic failure of the vessel. The NitRem process avoids this hazard.

As with many of the other technologies described in this report, there are limited data on toxicity of waste stream effluents, particularly for munitions-related waste streams, such as pink water, and some developed cost data are considered to be proprietary. However, due to the replaceable nature of the reaction vessel, costs are expected to be competitive with, or below, other SCWO processes. A joint program between Battelle and Sam Houston State University is currently in progress. The program plans include the construction of a transportable, palletized, NitRem pilot facility with 5 gpm capacity at Radford AAP. This plant will be available to treat waste streams at commercial process locations. 98,100

The vendor claims a cost of \$230/1,000 gal processed.⁹⁸ As a result, the NitRem process, like the other thermal processes, is not well suited to economically treat pink water.

The NitRem technology is compared with the reference GAC process in Bar Chart 4-9.* As can be seen, the NitRem process scores lower than GAC in all the performance criteria, except effluent quality.



4.4.5 Plasma Arc Technology

Plasma refers to the presence of ionized gases, and all electric arcs are plasmas. Plasma arc heaters are electrical resistance heaters in which the resistant element is the electrically-conductive, partially ionized gas between two electrodes. Plasma arc heaters provide a continuously-controlled electrical arc discharge. The control is achieved by magnetic and mechanical means, but a key design feature of plasma arc heaters is the controlled feed of gas to the arc environment. The electric arc furnace consists of an electrical power supply to create the arc and a system to control the gas flow and current to the electrodes. The gas supply is usually reducing (hydrogen), oxidizing (oxygen) or inert (argon). Additionally, the system uses a water-cooled torch, a furnace or cupola in which the reaction occurs, and pollution control equipment such as scrubbers, filters, and effluent stream monitoring equipment. Arc temperatures are generally in the range of 7,200° to 36,000°F, but the working temperature of the bulk gas is lower at about 3,600° to 5,400°F.

^{*} Evaluation methods and results are detailed in Section 5 and Section 6.

There are various producers of electric arc furnaces, and private industry is very active in this field of research. 101,102,103,104,105,106, 107,108 Additionally, laboratories operated by the Department of Energy (DOE), and the DOD, are actively working in the area of plasma arc technology and supporting research efforts elsewhere. 109,110,111 Most researchers are using the technology for high temperature metal heating, melting, re-melting, reclamation of scrap, treatment of ash from municipal solid waste incineration, medical waste treatment, and destruction of weapons components. 110,112,113,114 Only a few references were found for pollution abatement applications, and these were related to contaminated soils or relatively dry gas streams containing a target pollutant such as a VOC. 115,116

Injection of a water stream containing a pollutant (e.g. pink water wastes) at less than 1% solids does not appear to be a cost effective means of treatment. Indeed, such injection would have to proceed slowly to be able to adequately scrub the large quantities of steam generated. Typical equipment costs would be \$1 million for a 1 megawatt system and operating costs, including electricity, gas consumption (argon or oxygen) and consumables related to the torch, would be high. Rather than injecting a very dilute stream of pink water into a plasma arc, it would be more practical to inject GAC laden with explosives to reduce the volume of feed. However, when carbon destruction costs are included in overall operating cost, this adds \$2 to \$3/1,000 gallons of waste water just for GAC replacement. In summary, this process does not appear to be useful for pink water treatment.

4.4.6 Gas-Phase Hydrogen Reduction

This technology relies on gas-phase reduction with hydrogen gas at temperatures of 1,555° F.¹¹⁷ Despite the vendor's recommendation for process use on dilute water streams, this is generally an inappropriate application. Specifically, the energy requirements, capital costs, and safety issues associated with this process are significant. As a result, this process would compare very unfavorably with other alternatives for pink water treatment, had costs been available. High-temperature, high-pressure processes are generally too expensive to treat highly dilute streams like pink water.

4.5 Electron Beam Processing

A beam of accelerated electrons can break apart water molecules, forming energetic radicals, H° and OH°. These reducing and oxidizing radicals react with, and decompose, organic compounds. ^{118,119,120,121,122,123,124,125,126,127,128,129} Reaction products are relatively innocuous, such as carbon dioxide, NO_x, water and salts. The electron beam process (EBP) primarily produces potable drinking water by destroying trace organics, such as phenol, benzene, and toluene. Reactions of the electron-beam-produced species with organic molecules are very rapid, occurring in less than a second. This rapid reaction permits flow-through system designs operating at ambient pressure. Formation of reactive species is pH independent in the range of 3 to 11; as a result, variations in feed pH within this range will not affect the process.

The EBP is independent of feed temperature, and the waste-stream temperature normally increases only 1° to 2°F. Obviously, for dilute streams containing only a few hundred ppm of a target contaminant, like pink water, the lack of high temperature as a requirement for treatment can be a significant cost saving. The system is extremely versatile and the feed can be varied from aqueous streams to slurried soils, sludges, and sediments. Effluent from the process produces no organic sludge. There are no claimed hazardous air emissions, and in some cases the process effluent can be used as a pretreatment for another process. For example, complex organic molecules could be degraded into low molecular weight products that are more readily treatable by microbiological methods.

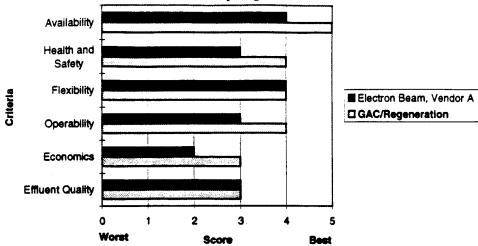
In practice, the electrons are generated in a beam about 0.8 inch in diameter. This beam is passed through a number of coils, which reshape the electron beam into a spray of electrons about 4 feet long and 2 inches wide. The beam then passes through two titanium windows and hits the water, which cascades over a thin weir. At 1.5 million volts and 50 mA, the electrons penetrate about 0.3 inch of water. Average conversion of electricity to chemical energy has been estimated to be about 65%, which increases to 85% at higher flow rates. Overall, the system has a relatively low net efficiency of between 33% and 44%. 120

EBPs require high capital investments and are relatively expensive to operate. 130,131 Vendor A predicts capital costs of \$1.72 million. Vendor B estimates \$3.2 million for capital expenditures. Vendor B has a transportable electron beam unit that is available for testing.

The Electron-Beam-Vendor-A technology is compared with the reference GAC process in Bar Chart 4-10. As can be seen, the Electron-Beam-Vendor-A process scores poorly in all the performance criteria, except effluent quality and flexibility where it equals GAC.

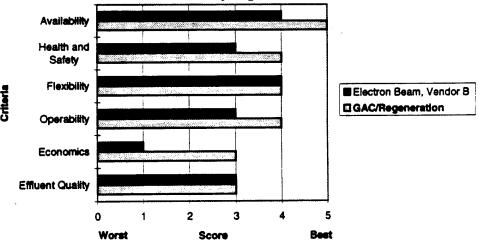
^{*} Evaluation methods and results are detailed in Section 5 and Section 6.

Bar Chart 4-10
Criteria Comparison Between Electron Beam, Vendor A and GAC
Followed by Regeneration



The Electron-Beam-Vendor-B technology is compared with the reference GAC process in Bar Chart 4-11. As can be seen, the Electron-Beam-Vendor-B process scores more poorly in all the performance criteria, except effluent quality and flexibility where it equals GAC.

Bar Chart 4-11
Criteria Comparison Between Electron Beam, Vendor B and GAC
Followed by Regeneration



^{*} Evaluation methods and results are detailed in Section 5 and Section 6.

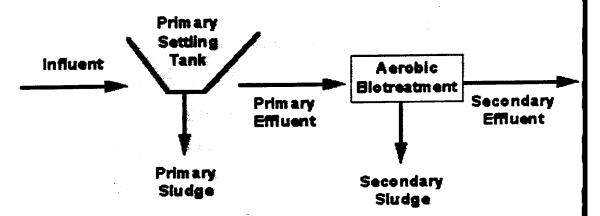
4.6 Biological

4.6.1 Background

Public Wastewater Treatment

In general, biological methods are the most common and least expensive treatments for liquid wastes. About 75% of the domestic wastewater treatment facilities in the U.S., approximately 12,000 plants, use the process shown schematically in Figure 4-1. After screening to remove debris, the influent enters a primary settling tank. Here insoluble materials and biomass settle to the bottom as primary sludge. Primary effluent is then pumped to aerated tanks where aerobic organisms consume and mineralize organic content. Biomass and insoluble materials settle out as secondary sludge. Approximately 20% of domestic treatment facilities further process secondary streams, for example, with anaerobic treatment. 132

Figure 4-1
Schematic of Conventional Primary and Secondary Wastewater Treatment



Wastewater treatment facilities usually exist in one of two common aerobic configurations:

- 1. Suspended-cell processes
 - a. Basins aerated by forced air
 - b. Lagoons aerated by stirrers,
- 2. Attached-cell processes
 - a. Trickling filters (packed beds in columns or stones in a water course)
 - b. Rotating biological contactors, a series of disks half immersed in a tank.

Anaerobic treatment is generally slower and less economical than aerobic treatment, and it is used either for supplementary or specialized processing. The major advantage of anaerobic versus aerobic treatment is the generation of less biomass. Other advantages related to specific uses are mentioned later.

In principle, the following specialized biological processes are similar to the large-scale plants described above.

Industrial Wastewater Treatment

The following model is a good starting point to characterize performance of specialized processes, including the technologies used for pink water. Aqueous organic compounds have four possible fates when subjected to biological treatment. Organic compounds can: 1) biodegrade, 2) volatilize, 3) associate with solids and precipitate, and 4) pass-through. The fates of organic compounds in conventional aerobic treatment have been estimated by a model with constants collected in a database. The model uses three constants:

- A biodegradation rate constant,
- Henry's Law Constant, and
- An octanol-water partition constant, which is correlated with water-sludge partitioning.

In a general sense, these parameters, which apply to conventional facilities, indicate the treatability of compounds by alternative, aerobic microbiological processes.

Specific technologies are grouped and described in the following paragraphs.

Granular Activated Carbon (GAC) Fixed Cell Technology Overview Because variants of fixed cell technology are described below, an introductory description is in order. The GAC, continuous-flow, column bioreactor, developed at the EPA's Risk Reduction Engineering Laboratory in Cincinnati, has many applications. The column usually operates with an up-flow feed, which expands and may fluidize the bed. In continuous flow, when contaminant concentrations exceed the biodegradation rate, the GAC adsorbs the excess. Thus, GAC accommodates concentration surges. After microbes reduce the dissolved concentration, the lowered liquid concentration causes contaminants to desorb from the carbon. Initially, the column may be fed with three streams, contaminated waste water, dilute activated sludge and a small amount of nutrients. Activated sludge contains an extraordinarily wide variety of microorganisms; eventually, organisms viable with the available carbon sources become resident. This process is effective in removing a

wide range of contaminants from waste waters. Columns also have been seeded with specific organisms to metabolize targeted compounds, and have been operated both aerobically and anaerobically. There are several variants of this technology, and examples follow.

Explosives Remediation

DOD priority contaminants were evaluated in a January 1994 report prepared for the NDCEE entitled, "Bioremedial Approaches to DOD Environmental Problems." The explosives category was reviewed with a focus on nitro-aromatic degradation organisms and their mechanisms. In addition, soil compositions at selected AAPs were reported.

Biological techniques have destroyed propellants and explosives, both in contaminated soils and in waste water streams. Soils have been treated mostly by composting. ^{135,136,137,138,139,140,141,142,143,144,145} However, rapid and complete degradation of energetics-contaminated soil slurries and waste water has been demonstrated in the laboratory. ¹⁴⁶ Waste water streams have been treated by biological methods, either alone or coupled with other techniques such as the PACT/WAO system. ^{80,147,148,149} Biological processes are widely used commercially for a variety of waste waters and sludges, as mentioned above, and reliable cost information is readily available.

4.6.2 Expanded-Bed GAC Anaerobic Bioreactor

DNT-contaminated waste water was treated in a continuous-flow, expanded-bed, GAC, anaerobic reactor. The reactor consisted of an 8-liter column, containing 6 liters of GAC fill, operated at a feed rate of 6 liters/day. Tests were performed both in the laboratory and the field. Field testing demonstrated effective destruction of DNT with influent varying from 76 ppm DNT to 165 ppm DNT. The product, diaminotoluene, was produced at roughly 80% or higher yield. Unfortunately, diaminotoluene, which has toxicity characteristics similar to TNT, is a suspected human carcinogen, as are amino-aromatics in general. However, a subsequent aerobic biological process might convert the amines to innocuous compounds.

Anaerobic reactors have a number of advantages compared to aerobic processes: lower sludge, more tolerance to toxics, no oxygen delivery costs, and the potential to produce methane, a useful byproduct. However, disadvantages include slow rates, sometimes by a factor of ten, and occasional production of toxic products, as reported above. Anaerobic GAC columns show destruction removal efficiencies frequently over 99%, and generally over 90%, with a large number of organic compounds. ¹⁵³

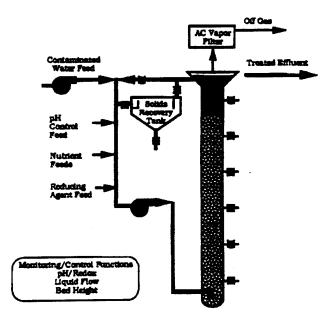
However, as noted above, compound destruction is not an achievement without knowledge of products produced. Expanded bed, GAC, anaerobic bioreactors show promise and warrant monitoring for further developments.

4.6.3 Anaerobic and Anaerobic-Aerobic Fluidized Bed Reactors

Anaerobic

The Fluidized Bed Reactor (FBR) is a minor variant of the previously described GAC technology. This fixed-film reactor consists of immobilized microbes on hydraulically fluidized media particles. The particles provide a large surface for biological film growth. Either sand or granular activated carbon can serve as the anchoring solid. GAC has added benefits because it adsorbs contaminants from solution and adds capacity to the system. Additional benefits are the FBR process's small size, mobility, and ease of operation. The known anaerobic product of TNT conversion is usually 2,4,6 triaminotoluene, a relatively toxic material. Figure 4-2 shows a typical FBR system.

Figure 4-2
A Typical Fluidized Bed Reactor Biological Treatment System



One vendor estimated a hydraulic residence time in the range of two to four hours, based on nitro-aromatic destruction tests with aqueous streams. ¹⁴⁸ Estimated capital costs were \$350,000.

The fluidized bed biological reactor technology is compared with the reference GAC process in Bar Chart 4-12. As can be seen, the Fluidized Bed Reactor process scores more poorly in all the performance criteria, except effluent quality and flexibility where it equals GAC. The effluent quality rating was based on vendor assurances.

Followed by Regeneration

Availability
Health and Safety
Flexibility
Operability
Economics
Effluent Quality

0 1 2 3 4 5
Worst Score Best

Bar Chart 4-12
Criteria Comparison Between Fluidized Bed Reactor and GAC
Followed by Regeneration

Anaerobic-Aerobic

A two-stage, Anaerobic-Aerobic, GAC FBR successfully treated a propellant waste stream containing 2,4-dinitrotoluene, as reported in a University of Cincinnati paper awaiting publication. The waste stream also contained ethanol, mineral ether, and carbonate buffer. The aerobic column mineralized the anaerobic-bioreactor product, primarily 2,4-diaminotoluene, within nine hours. The authors concluded that an FBR followed by aerobic treatment at an existing aerobic plant would be an effective strategy for the treatment of DNT waste. ¹⁵⁵

4.6.4 Aerobic GAC Cycling Batch Thermophilic Bioreactor

Under contract to the NDCEE, the Center for Hazardous Materials Research (CHMR) is developing microbial processes to destroy energetics-contaminated liquids and soils. The long-term goal is to scale up the technology and conduct a field demonstration. Although still being developed, the energetics-targeted, thermophilic organisms and the innovative processes to treat both soil slurries and liquids, are promising, as summarized below. 156

^{*} Evaluation methods and results are detailed in Section 5 and Section 6.

General Advantages of Thermophiles

Several inherent advantages of using thermophilic cultures are:

- Very rapid destruction of contaminants
- Minimal biomass production
- Organism growth at 130°F
- Naturally occurring organisms, inactive at ambient and body temperatures
- Technology already implemented for municipal waste treatment
- Generally applicable to all carbon-based compounds.

Feasibility Demonstration

A short-term demonstration, started in September 1994, accomplished the following:

- Isolated and developed 12 thermophilic cultures from energeticscontaminated soils from Crane, IN, and Umatilla, OR, ammunition processing facilities
- Acclimatized the cultures to completely degrade TNT and DNT at concentrations approaching water solubilities, in times ranging from 0.5 to 3.5 hours
- Completely destroyed target TNT and DNT compounds
- Tracked the disposition of products by radio-labeled testing
- Determined that the effluent was non-toxic by Microtox testing
- Designed processes to treat both aqueous solutions and soil slurries
- Evaluated process economics and showed cost and time advantages.

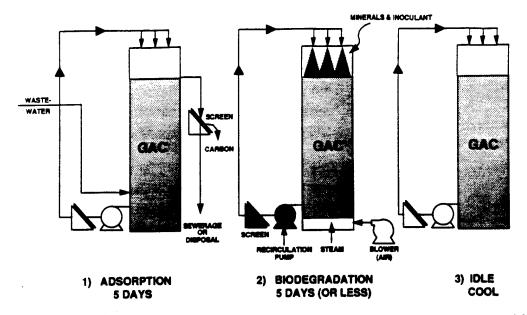
Process to Treat Pink Water

In a full-scale configuration, the proposed process is a modification of existing GAC equipment. Modification of existing equipment requires the addition of two flanges; one at the top of the column and one at the bottom. Some pipes connecting the flanges to a pump to recirculate the inoculant also would be required. These modifications can be done inexpensively in house by maintenance personnel.

After a conventional short loading cycle, Step 1, Figure 4-3, the GAC column starts biological treatment. Step 2, water in the column is circulated and heated to 130°F. Then inoculant and trace nutrients are added. Organisms feed on the nitrobodies, depleting the contaminants, thus regenerating the column. After flushing, the column enters Step 3, cool, idle, standby. Advantages of this process are:

- Uses existing equipment and the existing process, in part
- Low capital requirements
- Flexibility can tolerate surges and upsets in the loading cycle
- Comparable to current GAC process costs.

Figure 4-3
GAC, Cycling Batch Reactor Concept Using the Thermophilic Biological Process



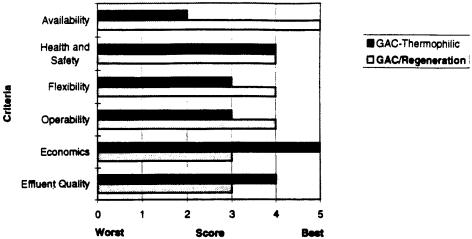
The proposed process is essentially the existing GAC process with in situ regeneration. One final point, organism development is at an early stage; based on history, significant performance improvement can be expected.

Because the process is new, many questions need answers. However, this application of thermophilic organisms to treat difficult wastes is innovative and may be used for other carbon-based contaminants. Because of its promise and many advantages, the GAC, Cycling Batch Bioreactor should be evaluated at the bench-scale.

The GAC with thermophilic biological regeneration technology is compared with the reference GAC process in Bar Chart 4-13. As can be seen, compared to the GAC reference, the thermophilic regeneration process scores higher in economics and effluent quality. However, the thermophilic process scores lower in commercial availability, flexibility and operability. Some of these poorer ratings could be argued. Unloading a carbon column seems more troublesome than an additional in situ operating step. Equal ratings in health and safety could also be argued on the same grounds. (However, incorporating these factors would not significantly affect the final rankings.)

^{*} Evaluation methods and results are detailed in Section 5 and Section 6.

Bar Chart 4-13
Criteria Comparison Between GAC-Thermophilic Processing and GAC Followed by Regeneration



4.6.5 Aerobic Rotating Biological Contactor

Researchers at the University of Tulsa demonstrated conversion of pink water TNT in a rotating biological contactor. The organism, Phanerochaete Chrysosporium (white-rot fungus) was immobilized on the disks of the contactor, which was operated in both a batch and continuous mode. Greater than 90% of the TNT was removed in a continuous reactor with a residence time of 24 hours. Disk area required was 10,000 ft²/gpm. RDX also could be treated at slower rates. The work did not detail the chemistry of the conversion products, but did provide detailed economics and design information.

The aerobic, rotating, biological contactor process consists of several unit operations, including final GAC treatment as a polishing step. Capital costs were estimated to be 3 to 4 times more than the standard GAC process. However, savings in operating costs of 20 to 25% of the standard GAC process, yielded a 12 to 18 month payback. Because the fungus was difficult to work with, the research focus shifted to direct use of the fungus' ligninase enzyme system. The enzyme work with porphyrins is reported in Section 4.6.6.

4.6.6 Aquatic Algae and Microbes

Algal Turf Scrubbing

A relatively new technology, developed at the Marine Systems Laboratory of the Smithsonian Institution, uses algae in ponds to scavenge nutrients from waste water. Because of the large number of highly developed species, these organisms are very efficient in assimilating a wide range of pollutants. Several full-scale commercial installations are operational,

primarily in California and Florida. A greenhouse installation, similar to the one described below, is planned for Lake Placid, New York.

Algae respire by taking in carbon dioxide and giving off oxygen as they use carbon to build cell mass. During this process, the organisms scavenge water for supplementary nutrients, absorbing and transforming a diverse group of compounds to the 10 ppb range. Although nitrogen and phosphorous compounds are preferred, algae have demonstrated removal of heavy metals as well as iron, magnesium, barium, manganese and calcium. A wide variety of organic compounds are reported to be absorbed, concentrated and transformed to varying degrees. The enzyme systems of micro-plants are similar to macrophytes (large plants). Destruction of pink water by macrophytes is described in a following section.

TNT was completely degraded in studies conducted at Clark-Atlanta University. However, results of radio-labeled studies were inconclusive and bench-scale work is continuing. In a configuration suitable for pink water treatment, this process might be visualized as two 500-feet-long by 10-feet-wide flow-ways in a heated greenhouse covered with double-walled polyethylene sheeting. Supplementary lighting, a harvester and a filter press are also necessary. As applied to pink water, this technology is in a relatively early stage of development and has significant limitations.

Algal processes have unique requirements:

- light and a warm environment (algae will not grow outside during northern winters.)
- continuous operation (relative to bacteria, algae are very slow growers.)
- biomass harvest and disposal or sale (dry biomass is valued at about \$0.20/lb. Harvesting and maintenance are labor intensive).

In addition, disposition of the energetic compounds removed from the water needs to be validated. For example, if the algae retain TNT-related compounds in the biomass, it would be both unfit for sale and possibly a disposal problem. Although potentially useful in a warm climate, close examination of utility costs for greenhouse lighting and heat eliminated this technology from those selected for detailed evaluation. This technology may find economical applications in a year-round, warm climate.

Mixed Microbial Mats

Microbial mats are naturally growing communities dominated by blue-green algae. These self-organized, laminated structures are tightly annealed together by slimy secretions. The surface slime effectively immobilizes the mat and stabilizes the internal structure. Because the mats are photosynthetic and nitrogen-fixing, they are solar-driven eco-systems with few growth requirements. Durable microbial mats will grow rapidly on ensiled grass clippings (silage). Constructed mats can address specific remedial problems if desired microbes are seeded in the blue-green algae and silage mixture. For example, co-cultured mats with white-rot fungus rapidly become a tightly-integrated, leathery unit covering the water surface.

A wide range of remedial applications are cited in the literature, including metals, and many organic compounds, including TNT. ^{160,161} Destruction percentage and rates for 100-ppm TNT were 99% in 6 days; for 217-ppm 2,4-DNT, these numbers were 88% in 4 days. ¹⁶² This technology shares the same warm weather requirement cited in the preceding section. Because of this limitation, detailed economics were not developed.

4.6.7 Large Aquatic Plants (Weeds)

Recent studies conducted at Rice University and the EPA's Athens Laboratory demonstrated that common aquatic weeds could be used to destroy energetic compounds. Current focus is on degradation pathways and factors affecting rates. Studies are being conducted in small laboratory equipment using weeds common to the Houston area and plant tissue cultures. Plants and tissue cultures not only survive, but may transform TNT into complex compounds in which TNT is not detectable by conventional analytical methods. Wetland, lagoon processes for treating wastes are well understood. The combination of this technology with plants that rapidly destroy energetic compounds is an alternative treatment for contaminated water.

A small-scale field demonstration is imminent at Alabama Army Ammunition Plant, Childersburg, Alabama. This inactive AAP, which produced TNT, DNT, and Tetryl powder in the past, is presently for sale. A small lagoon will use aquatic plants indigenous to the site to remediate highly contaminated soils. Leaching fields will be constructed to direct the leachate to the lagoon. Concentrations of leachate and lagoon will be monitored, and biomass concentrations will be maintained by harvesting excess growth.

Laboratory work indicates complete metabolism of saturated TNT solutions in less than 24 hours. Neither potential plant toxicity nor rate data are available for other pink water constituents. Based on the TNT-destruction rate and the 20-gpm pink water rate, projected active lagoon size is only 9,600 gallons, using an eight hour day for treatment.

Workers at Rice University have speculated that, even in a cold climate, one or two small lagoons, 100 feet by 100 feet by 3 feet deep, would adequately treat pink water at the 20 gpm rate. Based on analytical and radio-labeled studies of plant tissue, the only intermediate detected was 2,4-diamino-6-nitrotoluene at extremely low levels. Presumably, at steady-state the vegetation would eventually destroy the intermediate.

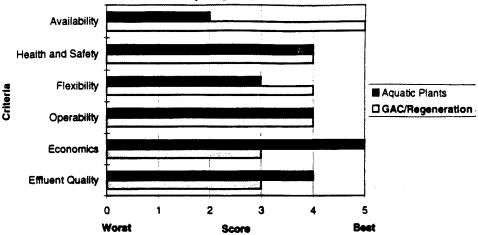
Although large and micro-plants share the same enzyme systems, as mentioned in a preceding section, there are important differences. For example, management of weeds and algae differ; harvesting is not an issue for weeds. Algae species are faster growing, far more diverse and responsive to change.

This work is in an early stage of development and has significant advantages which require development. More information is needed to define the process. Field experts suggest more detailed testing of this technology be performed in order to more adequately understand the reaction mechanism within the plants. 163

Processing of pink water with aquatic weeds in lagoons is compared with the reference GAC process in Bar Chart 4-14. As can be seen, the aquatic weeds technology scores better in economics and effluent quality, but scores more poorly in commercial availability and operability. The equal ratings in operability and health and safety could also be questioned. Lagoons, it could be argued, are easier and safer to operate than process equipment. (However, these changes would not significantly affect the final rankings.)

^{*} Evaluation methods and results are detailed in Section 5 and Section 6.

Bar Chart 4-14
Criteria Comparison Between Aquatic Plants and GAC Followed by Regeneration



4.6.8 Enzymatic Treatment

Background

Enzyme catalyzed chemistry is commonly used in industrial processing by fixing organisms and enzymes on surfaces. For example, a large-scale application is the conversion of corn syrup into the sweeter high-fructose syrup, commonly used in bottled beverages. Typically, batteries of columns 5 feet in diameter by 25 feet high may be packed with either organisms or enzymes fixed on diatomaceous earth. Corn syrup at a temperature of 140°F passes through the column and is partially converted to the sweeter isomer. The use of enzymes independent of life processes has advantages, including: 1) organisms can be independently grown under conditions to maximize enzyme production; 2) enzymatic changes can be optimized without being coupled to biological processes; 3) enzymes can be used under conditions that would not support life; and 4) chemical changes, unlike biological growth, are usually faster and can be turned on and off. This area is relatively undeveloped and has significant potential for contribution. An example of how this technology might apply follows. The major problem with enzyme systems is that extreme control of the influent constituents is necessary. Thus, although they work in production processes, they have difficulty in waste treatment processes.

Porphyrin Reduction of Nitro-aromatics

Porphyrins are metal-chelating ring structures often found at the active enzyme site in redox reactions. In the presence of reducing compounds, like dithiothreitol, sodium dithionate and sodium sulfide, porphyrins catalyze the conversion of nitro-aromatics to amines. Trivalent, cobalt-centered hematoporphyrin catalyzed the reduction of several nitrated toluene compounds, including TNT, to amines. Yields were generally in

excess of 90%.¹⁶⁵ The catalyst was immobilized on glass beads in a column 0.3-inch in diameter by 5 inches long. Economic projections were not made, but high porphyrin costs were suggested. However, commercial enzyme production typically reduces cost by orders of magnitude. Unfortunately, as discussed above, amino-aromatics in general are suspected human carcinogens. However, a subsequent biological process might be able to destroy the amines.

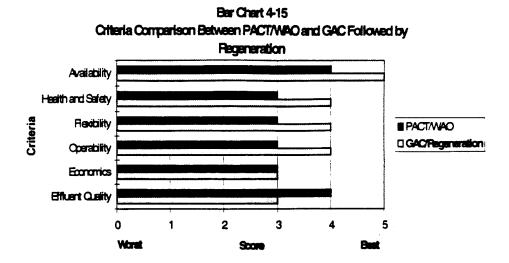
Although this very recent catalytic work is in an early stage of development, it bears watching. (Due to budget constraints, the Naval Civil Engineering Laboratory, which intended to fund continuing work, has put the project on hold.)

4.6.9 Combined Biological-Other Technologies

Combined technologies have been proposed to treat pink water; for example, biotreatment preceded or followed by other technologies. Because of accumulating cost, two-technology combinations are not likely to be as cost effective as single treatment processes. Examples of suggested technology combinations include base catalyzed hydrolysis and Powdered Activated Carbon Treatment (PACT®) with WAO or SCWO. WAO followed by PACT® biological treatment processes are commercially available as transportable units that can be used at customers' sites for field trials on waste streams from industrial processes. Tests conducted with pink water streams have shown a large reduction in COD and biochemical oxygen demand (BOD). Complete removal of the explosives could not be demonstrated because of analytical difficulties. One vendor estimates approximately \$300,000 in capital expenditures.

The PACT®/WAO process is compared with the reference GAC process in Bar Chart 4-15. As can be seen, the PACT®/WAO process scores lower than GAC in all criteria except effluent quality. The processes have an equal rating in economics.

^{*} Evaluation methods and results are detailed in Section 5 and Section 6.



4.7 Emerging Destruction Technologies

Two new technologies, sonication and microwave irradiation, have been identified as possible candidates for future bench-scale studies. Although the authors claim successful destruction of certain organic compounds, no data are available with respect to TNT, DNT, HMX, or RDX destruction.

Sonication

Ultrasonic waves in liquids produce and accelerate many chemical reactions. The waves create high temperatures and pressures in the liquid, in turn creating cavitating gas bubbles. These conditions cause thermal decomposition of the water; thereby forming hydroxyl radicals. Hydroxyl radicals, discussed in Section 4.2, are strong oxidizing agents, which react and destroy many organic compounds. Pyrolysis and radical reactions occur simultaneously and appear to be responsible for the destruction of p-nitrophenol in aqueous solution. The destruction of parathion by sonication also has been reported. 168

A vendor is in the process of scaling up a sonication process to enhance photocatalysis. ¹⁶⁹ In this application, ultrasonics primarily enhances mass transfer of the reactive species in the water. A pilot-scale system, funded by the DOE's Innovative Technologies Program, is under development.

Microwave Irradiation

Microwave irradiation in the presence of formate salts may be an effective way to destroy aromatics. R.S. Varma, in preliminary experiments, claims total disappearance of nitrobenzene within three minutes of treatment. The bath temperature under these conditions is 195 °F. Localized high temperatures are expected, presumably because of metallic species.¹⁷⁰

Similar results were obtained using activated carbon and simulating the conditions normally used in the regeneration of non-activated granular charcoal that had adsorbed nitrobodies from the pink water. No published data are available on these findings.

The technology originators claim:

- feasibility and scope of application of this innovative technology to pollution treatment by destroying or detoxifying common pollutants from munitions and demilitarization operations (nitroaromatics, nitramines, etc.), and
- adaptability to remediation efforts as applied to ground water contamination (nitrobodies, mercaptans, polychlorinated biphenyls, and dioxins).

Both of these processes are at early stages of development. Neither testing data nor cost estimations are available. At this point, no testing on pink water should be performed. However, further investigation into these processes may be warranted as they mature and if they show more promise associated with pink water treatment.

5.0 EVALUATION METHODS

This section describes the methods used to evaluate and rank the candidate pink water treatment technologies. The actual evaluation and discussion of results are in Section 6.

5.1 Selection Criteria

The following six selection criteria were used to screen the technologies that passed preliminary criteria screening for reasonableness and had adequate data to permit life-cycle cost analysis. The objective was to identify and recommend the five most promising technologies for bench-scale evaluation.

- 1. Effluent Quality weighs the probability that the process will comply with more stringent discharge limits. The toxicity of targeted pink water compounds and their conversion products were considered. Many technologies focus on destruction and fail to address conversion products, which may be more toxic than the starting materials.
- 2. **Process Operability** accounts for the complexity of the process, for example: Does the process require many operators? Must the operators be highly skilled or trained? Is the process difficult to control?
- 3. Process Flexibility concerns mobility of the process and functional aspects. for example: Can the process easily be shut down and started up? Can it be transported? Does it have capacity to accept changed operating conditions?
- 4. **Economics** are relative comparisons of life-cycle costs. As described below, this captures total process costs.
- 5. Commercial Availability judges the technical maturity of the technology, for example: Is the process readily available? How much experience is there with the process? If the process requires modification or further development, what is the likelihood of its success?
- 6. Health and Safety evaluates hazards associated with the process, for example: high-pressure, high-temperature caustic processes inherently carry greater risk than ambient, no-chemical processes.

5.2 Selection Process

Criteria Weighting

A panel of experts assigned weights to the listed criteria based on relative importance of the criteria to overall success. These weights are detailed in Table 5-1. Economics and Effluent Quality were thought to be the most important criteria, followed by Process Operability, then Process Flexibility and Health and Safety. Commercial availability received the lowest

weighting. Economics received a higher weighting than effluent quality because of uncertainties associated with effluent quality due to the lack of available data.

Table 5-1
Criteria Weighting for Pink Water Treatment Technology Evaluation

Selection Criteria	Weight, %
Economics	35
Effluent Quality	- 25
Process Operability	15
Process Flexibility	10
Health and Safety	10
Commercial Availability	5
Total	100

Criteria Scoring

The performance of each technology was scored on merit for each of the six criteria. Possible scores ranged from a high of 5 points to a low of 1 point for each criterion. Some processes that have uncertainty, especially within the effluent quality criterion, receive scores lower than that for GAC. This lower score does not mean that the effluent quality is necessarily worse but that further testing with pink water is required.

Weighted Scores

Weighted scores were calculated by multiplying each criterion score by the fractional criteria weight. The overall score for each technology was the sum of the weighted scores.

5.3 Process Economic Evaluation Methods

Because process economics were so important in the selection process, weighted at 35%, cost evaluation methods were carefully assessed.

Economic evaluations were based, in part, upon the material presented in Pamphlets 11-2, 11-3, and 11-4 mentioned in the contract Data Item Description sheet and MIL-STD-881, describing how to present life-cycle costs. Data Item Description DI-F-1215 describes the Life-Cycle Cost (LCC) Estimate as a prediction of the actual life-cycle cost of a system. The LCC is the total cost to the Government of acquisition and ownership. It includes the cost of development, acquisition, operation, support, and disposal.

5.3.1 Evaluation Methods and Selection

Several cost analysis methods were used to determine economic feasibility of the various pink water treatment options including:

- Pollution Prevention Financial Analysis and Cost Evaluation System (P2/Finance) provided by the EPA,
- EPA Total Cost Assessment,
- National Institute of Standards and Technology's Building Life Cycle Cost (BLCC) program, and
- Ranking of unit costs (\$/1,000 gallons).

These methods differ and the nuances were carefully weighed. For example, the BLCC program takes into account the time value of money, in addition to providing a total cost assessment. The BLCC program was selected as the most appropriate evaluation method. The BLCC program complies with the following:

- The American Society for Testing and Materials (ASTM) standard practices,
- The March 18, 1991 DOD Tri-Services memorandum of agreement on "Criteria/ Standards for Economic Analyses/Life Cycle Costing for MILCON Design, and
- OMB Circular A-94 (revised), "Guidelines and Discount Rates for Benefit-Cost Analysis of Federal Programs," October 29, 1992.

5.3.2 Life-Cycle Cost Analysis Using the BLCC Program

All of the pink water treatment alternatives were evaluated using the BLCC program, which calculates present values for cash-flow streams. Alternatives were evaluated to determine life cycle cost, which measures long-run economics.

LCC analysis is a decision-making tool for choosing among alternatives based on long-run economic performance, rather than initial cost. The method sums costs of initial investment, capital replacements, operating, maintenance, and repair (OM&R), including non-capital replacements, and energy over a given study period. The LCC is usually expressed in either present value or annual value dollars. These numbers are adjusted for the time value of money using the discount rate. This report shows present-value (PV) dollars over a 15 year performance period.

A table of complete cost estimates is provided in the Appendix for each of the pink water treatment options. These estimates were obtained from research centers, vendors, field experts and engineering estimates. From these tables, the total capital cost and total operating cost were input to the BLCC model.

In addition, the following factors or assumptions were used in the analysis:

- 15 year project life,
- 8% discount factor,
- exclusion of inflation, and
- exclusion of depreciation.

6.0 TECHNOLOGY SELECTION

6.1 Economic Evaluation

6.1.1 Source Data and Models

Research centers, vendors, and field experts were solicited to supply process economic data based on the operating specifications. These sources contributed the operating and capital costs detailed in spreadsheets, used to model economics for processes. These spreadsheets are provided and described in Appendix A, and the important results are summarized in Table 6-1. However, all processes described in preceding sections were not analyzed. If processes were either extremely costly or data were unavailable, a detailed analysis was not performed.

Process specifications included a 20 gallon per minute flow rate, a total initial concentration of explosives of 200 ppm, and a final concentration of 0.25 ppm. As a baseline, cost data for GAC adsorption followed by off site incineration, or carbon adsorption followed by off site regeneration, were produced.

Table 6-1 Capital Cost and Annual Operating Cost Data for Alternative Pink Water Treatment Technologies Summarized From Appendix A

	Discussed in	Capital	Annual Operating
Technology	Section	Costs, \$	Costs, \$
BASE CASE	3.1	159,900	48,100
GAC/Off-site Incineration			30.500
BASE CASE	3.1	159,900	30,700
Carbon/Off-site Regeneration	<u> </u>		
Advanced Oxidation Process, Vendor A	4.2.2	184,500	35,000
Advanced Oxidation Process, Vendor B	4.2.3	492,000	27,000
Fenton's Chemistry	4.2.4	215,250	30,800
Electrolytic, Vendor A	4.3.1	101,500	30,500
Electrolytic, Vendor B	4.3.2	307,500	147,000
Hydrothermal Processing			
Wet Air Oxidation (WAO)	4.4.2	3,000,000	264,000
Supercrit. Water Oxidation, Vendor A	4.4.3	2,091,000	209,000
Supercrit. Water Oxidation, Vendor B	4.4.3	2,152,000	241,200
GAC with SCWO	4.4.3	707,250	87,300
NitRem	4.4.4	5,608,800	351,440
	4.5	1,722,000	94,970
Electron Beam, Vendor A	4.5	3,198,000	179,500
Electron Beam, Vendor B	4.3	3,170,000	177,500
Biological			
Fluidized Bed Bioreactor	4.6.3	356,700	32,400
Powdered Carbon with WAO	4.6.9	307,500	54,500
GAC Thermophilic	4.6.4	174,600	21,000
Large Aquatic Plants	4.6.7	184,500	9,700

6.1.2 Life-Cycle Cost Analysis

Uninflated GAC Cost

As noted in preceding sections, pink water treatment technologies were evaluated using life-cycle cost analysis. The life-cycle costs in Table 6-2 reflect the "Government" method of economic evaluation including long-term bond discount rates (i.e. the January 24, 1995 rate of 8%), and exclusion of depreciation, insurance and overhead costs. Of the 16 alternatives, five processes have LCCs between \$270,000 and \$480,000. This compares favorably to off-site incineration and off-site thermal regeneration, which respectively have LCCs of \$572,000 and \$423,000. Based on LCC data, there are five technology alternatives to the current DOD practices that would be economically feasible. Three have lower LCCs than either thermal regeneration or incineration; while all five have lower LCCs than incineration.

Table 6-2
Life-Cycle Costs for Pink Water Treatment Alternative Technologies

			Capital	Life Cycle
Rank	Technology	Section	Cost (\$, PV)	Cost (\$, PV)
1	Large Aquatic Plants	4.6.7	184,500	267,424
2	GAC Thermophilic Process	4.6.4	171,900	341,489
3	Electrolytic, Vendor A	4.3.1	101,500	362,479
4	BASE CASE - GAC/Regeneration	3.1	159,900	422,727
5	Fenton's Chemistry	4.2.4	215,250	479,575
6	Advanced Oxidation Process, Vendor A	4.2.2	184,500	484,227
7	BASE CASE - GAC/Incineration	3.1	159,900	571,662
8	Fluidized Bed Bioreactor	4.6.3	- 356,700	634,027
9	Advanced Oxidation Process, Vendor B	4.2.3	492,000	723,782
10	Powdered Carbon with Wet Air Oxidation	4.6.9	307,500	774,420
11	GAC with Supercrit. Water Oxidation	4.4.3	707,250	1,453,954
12	Electrolytic, Vendor B	4.3.2	307,500	1,565,847
13	Electron Beam, Vendor A	4.5	1,722,000	2,533,011
14	Supercrit. Water Oxidation, Vendor A	4.4.3	2,091,000	3,880,146
15	Supercrit. Water Oxidation, Vendor B	4.4.3	2,152,500	4,216,833
16	Electron Beam, Vendor B	4.5	3,198,000	4,733,999
17	Wet Air Oxidation	4.4.2	3,000,000	5,259,703
18	NitRem	4.4.4	5,608,800	8,616,944

Note: PV = Present Value

Inflated GAC Cost

A driver behind this project is the expected increase in carbon treatment costs. Therefore, Table 6-3 presents a 10 percent escalation factor for both the GAC with Off-site Thermal Regeneration and GAC with Off-site Incineration processes. With this assumption, six of the 16 pink water alternatives have lower LCCs than the base case of GAC/Regeneration, and eight have lower LCCs than the base case of GAC/Incineration.

With the escalation of the base cases, the LCC for off-site thermal regeneration and off-site incineration more than increases by approximately 40 percent to \$694,993 and \$998,211, respectively. As a result, three additional technologies have LCC lower than the escalated LCC for the current DOD practices. Since cost escalation seems to be the most realistic situation, economic scoring used in the selection process focused on the LCC data given in Table 6-3 as a basis.

Table 6-3
Life-Cycle Costs for Pink Water Treatment Alternative Technologies:
10% Escalated Base Cases

Rank	Technology	Section	Capital Cost (\$, PV)	Life Cycle Cost (\$, PV)	Score
	Large Aquatic Plants	4.6.7	184,500	267,424	5
2	GAC Thermophilic Process	4.6.4	171,900	341,489	5
3	Electrolytic, Vendor A	4.3.1	101,500	362,479	5
4	Fenton's Chemistry	4.2.4	215,250	479,575	5
5	Advanced Oxidation Process (AOP) Vendor A	4.2.2	184,500	484,227	5
6	Fluidized Bed Bioreactor	4.6.3	356,700	634,027	4
7	INFLATED BASE CASE - GAC/Regeneration	3.1	159,900	694,993	4
8	Advanced Oxidation Process (AOP) Vendor B	4.2.3	492,000	723,782	3
9	Powdered Carbon with Wet Air Oxidation	4.6.9	307,500	774,420	3
10	INFLATED BASE CASE - GAC/Incineration	3.1	159,900	998,211	2
11	GAC with Supercrit. Water Oxidation	4.4.3	707,250	1,453,954	2
12	Electrolytic, Vendor B	4.3.2	307,500	1,565,847	2
13	Electron Beam, Vendor A	4.5	1,722,000	2,533,011	2
14	Supercrit. Water Oxidation (SCWO) Vendor A	4.4.3	2,091,000	3,880,146	1
15	Supercrit. Water Oxidation (SCWO) Vendor B	4.4.3	2,152,500	4,216,833	l
16	Electron Beam, Vendor B	4.5	3,198,000	4,733,999	1
17	Wet Air Oxidation	4.4.2	3,000,000	5,259,703	1
18	NitRem	4.4.4	5,608,800	8,616,944	1

Note: PV = Present Value

Economic Evaluation Conclusions

Because of escalating permitting and disposal costs, Table 6-3 more realistically compares the current technology with replacement alternatives. The only difference between Table 6-2 and Table 6-3 is the relative position of the currently used GAC processes. The relative positions of the other technologies are unchanged.

The LCCs in Table 6-3 were grouped and ranked. Evidently, formal statistical methodologies do not exist to treat this specific grouping process. As a result, the highest and lowest cost were arbitrarily assigned values of 5 and 1, respectively. The distribution was then divided into quintiles.

Eight of the alternative processes are economically feasible when compared to the base cases of GAC/Incineration and GAC/Regeneration. All eight of the alternatives with lower LCCs than the base cases also have initial capital investments under \$500,000.

6.2 Other Criteria Scoring and Evaluation

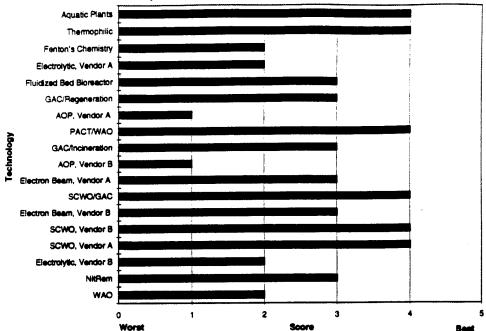
As described in Section 5.2, each technology was scored on a scale of 5, best, to 1, worst, in each of the six criteria. A panel familiar with the technologies scored each process independently, and then reached a consensus on the scores.

Uncertainty played a major role in scoring the five remaining criteria. Definitive data for pink water were generally unavailable, and some technologies did not have data on related compounds. Available data and plausible extrapolation were the foundation for the technical judgments that scored each criterion.

Effluent Quality Scoring

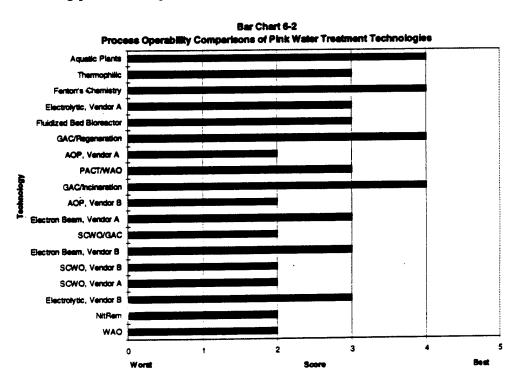
The reference GAC technologies scored 3 in effluent quality, because they do not destroy the energetic wastes, and result in a disposal problem, see Bar Chart 6-1. The highly scored technologies provided evidence that they could destroy pink water contaminants. Lower scored alternatives had more questionable capabilities. For example, if run anaerobically, the GAC fluidized bed bioreactor will likely produce 2,4,6-triaminotoluene, although the vendor claims otherwise. As a result, this technology scored 3. Technologies that scored lower had increasing performance questions.

Bar Chart 6-1
Effluent Quality Comparisons of Pink Water Treatment Technologies



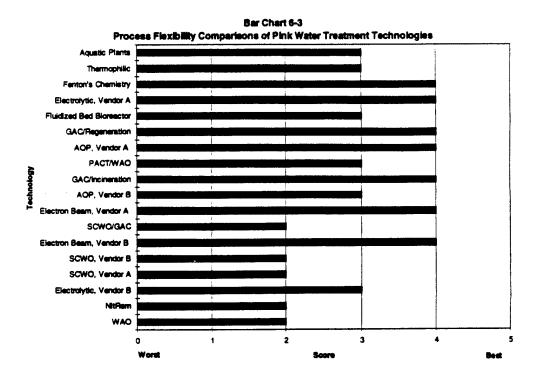
Process Operability Scoring

The reference GAC technologies scored 4 in operability, because they are relatively simple, existing processes, see Bar Chart 6-2. Other highly scored technologies, Fenton's chemistry and aquatic plants, are relatively easy to operate. Increasing process complexity resulted in lower scores.



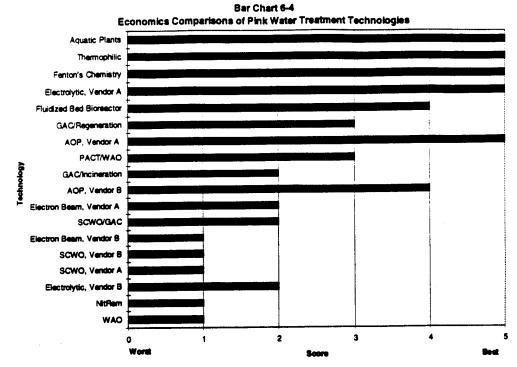
Process Flexibility Scoring

The reference GAC technologies scored 4 in flexibility, because they are relatively simple, easily set-up processes, and capable of accepting a range of feed concentrations, see Bar Chart 6-3. Other highly scored technologies are Fenton's Chemistry, Electron Beam, and AOP Vendor A; these technologies were palletized or relatively portable. High-pressure, high-temperature processes scored lowest because of restrictions on feed rates and more involved set-up.



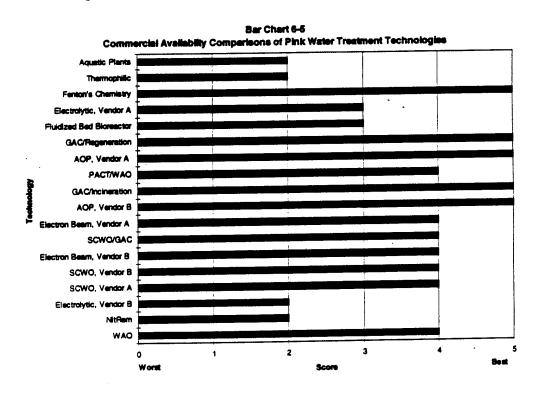
Process Economics Scoring

Bar Chart 6-4 is based on the life-cycle costs from Table 6.3. The reference GAC technologies scored in the mid-range of life-cycle costs. Other highly scored technologies are Aquatic Plants, Thermophilic, Fenton's Chemistry, Electrolytic, Vendor A and AOP. High-pressure, high-temperature processes were costly to install and operate; this accounts for their low scores in this important criterion.



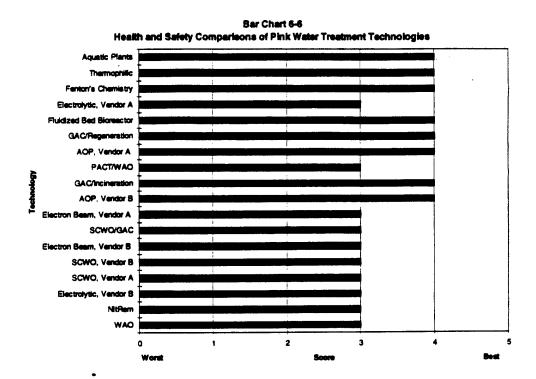
Commercial Availability Scoring

Of course, the reference GAC technologies scored 5 in commercial availability, see Bar Chart 6-5. Other highly scored readily available commercial technologies are Fenton's Chemistry and the two advanced oxidation processes. Scores for developing technologies were lower, depending on the state of development and ease of implementation.



Health and Safety Scoring

The reference GAC technologies scored 4 in health and safety, Bar Chart 6-6. Handling of carbon loaded with energetic compounds contributed to this score. Uncertainties down-rated the biological processes, which may eventually prove themselves among the safest. The spread in scoring is relatively narrow, and an argument could be made to down-rate the high-pressure, high-temperature processes. (Because all of these technologies ranked near the bottom on total score, this would not change the final results.)



6.3 Ranking of Alternative Technologies

Criteria scoring results described in the preceding section are summarized in Table 6-4. These scores are multiplied by the fractional weights for each criterion, listed in Table 5-1. A total score for each technology is the sum of the weighted criteria scores. Resulting total scores are shown in a descending order, with the best at the top, in Table 6-5.

Table 6-4
Scoring of Pink Water Treatment Methods

				Criteria	and Scores		
		Effluent	Process	Process		Commercial	Health and
Section	Candidate	Quality	Operability	Flexibility	Economics	Availability	Safety
3.1	GAC/Incineration	3	4	4	2	5	4
3.1	GAC/Regeneration	3	4	4	3	5	4
					r		Γ
4.2.2	AOP, Vendor A	1	2	4	5	5	4
4.2.3	AOP, Vendor B	1	2	3	4	5	4
4.2.4	Fenton's Chemistry	2	4	4	5	5	4
4.3.1	Electrolytic, Vendor A	2	3	4	5	3	3
4.3.2	Electrolytic, Vendor B	2	3	3	2	2	3
4.4.2	WAO	2	2	2	1	4	3
4.4.3	SCWO, Vendor A	4	2	2	1	4	3
4.4.3	SCWO, Vendor B	4	2	2	11	4	3
4.4.3	GAC with SCWO	4	2	2	2	4	3
4.4.4	NitRem	3	2	2	1	2	3
							T
4.5	Electron Beam, Vendor A	3	3	4	2	4	3
4.5	Electron Beam, Vendor B	3	3	4	1	4	3
4.6.3	Fluidized Bed Reactor	3	3	3	4	3	4
4.6.4	Thermophilic	4	3	3	5.	2	4
4.6.7	Large Aquatic Plants	4	4	3	5	2	4
4.6.9	Powdered Carbon with WAO	4	3	3	3	4	3

Table 6-5
Total Scores for Pink Water Alternative Treatment Technologies

Section	Candidate	Total Score
4.6.7	Large Aquatic Plants	4.15
4.6.4	GAC Thermophilic	4.00
4.2.4	Fenton's Chemistry	3.90
4.3.1	Electrolytic, Vendor A	3.55
4.6.3	Fluidized Bed Bioreactor	3.45
3.1	GAC/Regeneration	3.45
4.2.2	AOP, Vendor A	3.35
4.6.9	PACT/WAO	3.30
3.1	GAC/Incineration	3.10
4.3.2	AOP, Vendor B	2.90
4.5	Electron Beam, Vendor A	2.80
4.4.3	SCWO/GAC	2.70
4.5	Electron Beam, Vendor B	2.45
4.3.2	Electrolytic, Vendor B	2.35
4.4.3	SCWO, Vendor A	2.35
4.4.3	SCWO, Vendor B	2.35
4.4.4	NitRem	2.00
4.4.2	Wet Air Oxidation	1.85

Based on these calculations, the top five candidate alternative technologies are:

- 1. Large Aquatic Plants Treatment
- 2. GAC Thermophilic Process
- 3. Fenton's Chemistry Process
- 4. Electrolytic Process, Vendor A
- 5. Fluidized Bed Bioreactor Process.

These top five treatment technologies were selected because of their perceived ability to treat pink water to within discharge limits. In addition, these processes do not involve large capital expenditures. Vendors claim these processes require relatively little labor, maintenance, and utilities, making them fairly inexpensive to operate. As far as engineering functionality is concerned, portability, flexibility, and availability were considered most important. These processes fall within all of the above functional criteria better than other evaluated processes, as demonstrated by their high total scores. Vendors contacted indicated that they would cooperate in adapting and/or optimizing their processes for effectively treating pink water. Effluent toxicity data were not available for most of the above processes.

Toxicity data can be obtained with bench scale testing. Although the above evaluation process was quantitative and thorough, it was based on the best available data and some engineering judgment. For example, the Electrolytic, Vendor-A process scored more highly than perhaps is justified. The greatest uncertainty in the scoring was the Effluent Quality criterion. Much of this input was speculative, dependent on experience and engineering judgment. Thus, a technology with low cost and other desirable characteristics might appear near the top of the list, even with uncertain effluent characteristics. As a result, the demonstration of effluent quality (not compound destruction) needs to be among the first priorities for all technologies.

7.0 CONCLUSIONS

Based on the review of candidate technologies for treating pink water, and applying the evaluation criteria to rank the candidates, the following conclusions may be made.

- 1. Destruction technologies have the ability to eliminate discharge problems.
- 2. Selected destruction technologies are cost competitive with traditional GAC treatment with thermal regeneration.
- 3. The five technologies listed below are currently the best candidates for pink water destruction, and should be investigated at the bench scale:
 - Large Aquatic Plants (Biological) Treatment
 - GAC Thermophilic (Biological) Process
 - Fenton's Chemistry (AOP) Process
 - Electrolytic Process, Vendor A
 - Fluidized Bed Bioreactor Process.
- 4. Process performance needs to be validated by analysis of products formed. Some technologies may destroy the targeted pink water compounds, but may produce toxic reaction products. Effluent toxicity evaluation should be a key task in Phase 2.

8.0 RECOMMENDATIONS

After selection approval of the five best alternative destruction technology candidates, Phase 2 should proceed. Activities to be undertaken should include the following:

- 1. Perform bench scale testing and evaluations on the five best technologies.
- 2. Use identical pink water samples for testing under identical conditions.
- 3. Select pink water samples for testing from two different operations; one from LAP plants, and the other from demilitarization operations.
- 4. Address permit considerations at the earliest opportunity. Vendors shall be responsible for determination of the required permits and work with their facility staff or AAP facility staff to ensure that bench-scale testing can proceed without delay.
- 5. The NDCEE and USAEC team should monitor the bench-scale tests.
- 6. The NDCEE and USAEC team should validate the test results from the bench-scale tests.
- 7. Perform analytical testing at a single laboratory approved by the NDCEE and USAEC. If technology owners want to perform their own tests, sample splits should be analyzed by the same methods used by the primary laboratory.
- 8. Perform toxicity tests on all effluents generated by each alternative technology.
- 9. Perform an updated economic feasibility study on each technology tested at bench scale.
- 10. Select three of the five technologies evaluated for scale-up and testing at the pilot plant size.
- 11. Investigate pollution prevention opportunities available at AAPs as an alternative to employing the best candidate destruction technologies.

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APPENDIX

TABLE A-1 Capital and Annual Operating Cost Data for: Advanced Oxidation Process, Vendor A

PRIMARY OPERATING DATA

Operations

Davs

250 days/yr

hr/yr

hr/shift

Shifts

1 shift/day

2,000

8

No. of Operators 0.25 operators/shift

Pink Water

Flowrate

20 gpm

Initial Concentration Final Concentration

200 ppm 0.25 ppm

Electricity

Supervision

Overhead

Other

9,600 gpd

2,400,000 gpy

COST DATA

Capital Costs

Contingency Working Capital 3 % Fixed Capital

20 % Fixed Capital

0.10 \$/kW-hr 10 % Electric

25 % Labor and Maint

30 % Labor and Maint

Direct Expenses

Operator Labor Maintenance 10 \$/hr

2 % Fixed Capital

Supplies **Materials** 10 % Maintenance 3 % Fixed Capital

Lab Charges

10 % Labor

Special Materials

Hydrogen Peroxide

0.008 \$/ppm/1000gal

H2O2 conc.

150 ppm

OPERATING COSTS

Indirect Expenses

CAPITAL COSTS

Fixed Capital (includes installation)

150,000

Raw Materials (Includes H2O2 and bulbs) Utilities (Vendor Estimate)

12,420 9,197 5,000

Contingency (3% Fixed Capital)

4,500

Labor Maintenance (2% Fixed Capital) Lab Charges (10% Labor)

3,000 500

Working Capital (20% Fixed Capital)

30,000

Supplies (10% Maintenace) Supervision (25% Labor & Maintenance)

Overhead (30% Labor & Maintenance)

500 2,000 2,400

TOTAL Capital Costs:

184,500

TOTAL: Operating Costs

TABLE A-2 Capital and Annual Operating Cost Data for: Advanced Oxidation Process, Vendor B

PRIMARY OPERATING DATA

Operations

Davs 250 days/yr

Shifts

1 shift/day

hr/yr 2,000 hr/shift

No. of Operators

0.2 operators/shift

Pink Water

Flowrate

20 gpm -

9,600 gpd 2,400,000 gpy

initial Concentration

200 ppm

Final Concentration

0.25 ppm

COST DATA

Capital Costs

Contingency Working Capital 3 % Fixed Capital

20 % Fixed Capital

Utilities

Electricity

0.10 \$/kW-hr

Other

10 % Electric

Direct Expenses

Operator Labor

TOTAL Capital Costs:

10 \$/hr

Maintenance Supplies

2 % Fixed Capital 10 % Maintenance

Materials

1 % Fixed Capital

Lab Charges

10 % Labor

Indirect Expenses

Supervision Overhead 25 % Labor and Maint

30 % Labor and Maint

OPERATING COSTS . CAPITAL COSTS 4,000 Raw Materials 400,000 Fixed Capital (includes installation) 3,679 Utilities (Vendor Estimate) 4,000 12,000 Labor Contingency (3% Fixed Capital) 8,000 Maintenance (2% Fixed Capital) 400 Lab Charges (10% Labor) 80,000 Working Capital (20% Fixed Capital) 400 Supplies (10% Maintenance) Supervision (25% Labor & Maintenance) 3,000 Overhead (30% Labor & Maintenance) 3,600 27.079 492,000 **TOTAL Operating Costs**

TABLE A-3 Capital and Annual Operating Cost Data for: Fenton's Chemistry

PRIMARY OPERATING DATA

Operations

Davs

250 days/yr

1 shift/day

hr/yr 2,000 hr/shift

8

Shifts No. of Operators

0.2 operators/shift

Pink Water

Flowrate

20 gpm

Initiat Concentration

200 ppm

9,600 gpd

2,400,000 gpy

Final Concentration

0.25 ppm

COST DATA

Capital Costs

Contingency Working Capital

3 % Fixed Capital 20 % Fixed Capital Utilities

Electricity

0.10 \$/kW-hr

10 % Electric Other

Direct Expenses

Operator Labor Maintenance

10 \$/hr

2 % Fixed Capital

Supplies

10 % Maintenance 2 % Fixed Capital

Materials Lab Charges

10 % Labor

Indirect Expenses

Supervision

25 % Labor and Maint

Overhead

30 % Labor and Maint

Special Materials

H2O2 conc

300 ppm

Hydrogen Peroxide

0.008 \$/ppm/1000gal

OPERATING COSTS CAPITAL COSTS

Fixed Capital (includes installation)

175,000

9,260 Raw Materials 9,197 Utilities (Estimate) 4,000

Contingency (3% Fixed Capital)

Working Capital (20% Fixed Capital)

5.250 35,000 Labor Maintenance (2% Fixed Capital)

Overhead (30% Labor & Maintenance)

400 Lab Charges (10% Labor) Supplies (10% Maintenance) 400 Supervision (25% Labor & Maintenance) 1,875

TOTAL Capital Costs:

215,250

TOTAL Operating Costs

30,882

2.250

TABLE A-4 Capital and Annual Operating Cost Data for: Electrolytic, Vendor A

PRIMARY OPERATING DATA

Operations

250 days/yr Days

hr/yr 2.000 hr/shift

Shifts No. of Operators

1 shift/day 0.25 operators/shift

Pink Water

Flowrate

20 gpm 1

Initial Concentration

200 ppm

9,600 gpd

2,400,000 gpy

Final Concentration

0.25 ppm

COST DATA

Capital Costs

Contingency Working Capital

3 % Fixed Capital 100 % Fixed Capital Utilities

Electricity

Supervision

Overhead

0.10 \$/kW-hr

Other

10 % Electric

Direct Expenses

Operator Labor

10 \$/hr

0.18 \$/gat

Indirect Expenses

Maintenance Supplies 4 % Fixed Capital

Materials

SCOLA

10 % Maintenance 3.2 % Fixed Capital

Lab Charges

10 % Labor

Process Specific Calculations Power Rea'd:

0.30 kW-hr/ 40 gal SCOLA

25 % Labor and Maint

30 % Labor and Maint

SCOLA Production:

40 gph

Electrical Cost:

80,000 gpy 2,400 \$/yr

CAPITAL COSTS

Special Materials

Fixed Capital (includes installation)

50,000

OPERATING COSTS

16,000

Contingency (3% Fixed Capital)

1,500

Raw Materials Utilities (Vendor Estimate) Labor

2,640 5,000

Maintenance (4% Fixed Capital) Lab Charges (10% Labor)

2.000 500

Working Capital (100% Fixed Capital)

50,000

Supplies (10% Maintenance) Supervision (25% Labor & Maintenance) Overhead (30% Labor & Maintenance)

500 1,750 2.100

TOTAL Capital Costs:

101,500

TOTAL Operating Costs

TABLE A-5 Capital and Annual Operating Cost Data for: Electrolytic, Vendor B

PRIMARY OPERATING DATA

Operations

Days

250 days/yr

1 shift/day

hr/yr

hr/shift

Shifts No. of Operators

0.25 operators/shift

2,000

8

Pink Water

Flowrate

20 gpm

Initial Concentration

200 ppm

9,600 gpd 2,400,000 gpy

Final Concentration

0.25 ppm

COST DATA

Capital Costs

Contingency Working Capital 3 % Fixed Capital

20 % Fixed Capital

I Hillian

Electricity

0.10 \$/kW-hr

Other

10 % Electric

Direct Expenses

Operator Labor

10 \$/hr

Maintenance

2 % Fixed Capital

Supplies **Materials** 10 % Maintenance 2 % Fixed Capital

Lab Charges

10 % Labor

Indirect Expenses

Supervision Overhead 25 % Labor and Maint

30 % Labor and Maint

Process Specific Calculations

Power Reg'd=

0.36 kW-hr/gal

Electrical Cost =

85,920 \$/yr

Electrode Change-Out=

20,000 \$/yr

CAPITAL COSTS

OPERATING COSTS

Fixed Capital (includes installation)

250,000

Raw Materials Utilities (Vendor Estimate) 5,000

Contingency (3% Fixed Capital)

7,500

Labor Maintenance (2% Fixed Capital)

Supervision (25% Labor & Maintenance)

Overhead (30% Labor & Maintenance)

94.512 5,000

Working Capital (20% Fixed Capital)

50.000

Lab Charges (10% Labor) Supplies (10% Maintenance) 25.000 500 500i 7.500

9.000

TOTAL Capital Costs:

307,500

TOTAL Operating Costs

TABLE A-6 Capital and Annual Operating Cost Data for: **GAC** with Supercritical Water Oxidation

PRIMARY OPERATING DATA

Operations

Days

250 days/yr 1 shift/day hr/yr

hr/shift

Shifts No. of Operators

0.5 operators/shift

2,000

8

Pink Water

Flowrate

20 gpm

Initial Concentration Final Concentration

200 ppm 0.25 ppm

9,600 gpd

2,400,000 gpy

COST DATA

Capital Costs

Contingency Working Capital 3 % Fixed Capital

20 % Fixed Capital

Utilities

Indirect Expenses

Electricity

Supervision

Overhead

0.10 \$/kW-hr

Natural Gas

6 \$/1000 SCF

25 % Labor and Maint

30 % Labor and Maint

Water 0.01 \$/gat

Direct Expenses

Operator Labor

10 \$/hr

Maintenance Supplies 3 % Fixed Capital

Materials

10 % Maintenance 4 % Fixed Capital

Lab Charges

10 % Labor

Special Materials

Carbon

Cost

13.000 lb/yr 1.00 \$/lb

CAPITAL COSTS

575,000

OPERATING COSTS Raw Materials

36,000

Contingency (3% Fixed Capital)

17,250

Utilities (Vendor Estimate) Labor

7,000 10,000 17,250

Working Capital (20% Fixed Capital)

Fixed Capital (includes installation)

115,000

Maintenance (3% Fixed Capital) Lab Charges (10% Labor) Supplies (10% Maintenance) Supervision (25% Labor & Maintenance)

Overhead (30% Labor & Maintenance)

1,000 1,000 6,813

TOTAL Capital Costs:

707,250

TOTAL Operating Costs

87,238

8.175

TABLE A-7 Capital and Annual Operating Cost Data for: Supercritical Water Oxidation, Vendor A

PRIMARY OPERATING DATA

Operations

Days Shifts 250 days/yr 1 shift/day

hr/shift hr/yr 2,000

8

No. of Operators

0.33 operators/shift

Pink Water

Flowrate

20 gpm

Initial Concentration

200 ppm

9.600 gpd 2,400,000 gpy

Final Concentration

0.25 ppm

COST DATA

Capital Costs

Contingency **Working Capital** 3 % Fixed Capital

20 % Fixed Capital

Utilities

Electricity

0.10 \$/kW-hr

Naturai Gas

6 \$/1000 SCF

Water 0.01 \$/gal

Direct Expenses

Operator Labor Maintenance 10 \$/hr

3 % Fixed Capital

Supplies |

10 % Maintenance 2 % Fixed Capital

Materials Lab Charges

10 % Labor

Indirect Expenses

Supervision

25 % Labor and Maint

Overhead

30 % Labor and Maint

Special Materials

#2 Fuel Oil

430 lb/d

Process Specific Calculations

Gas Requirements:

300,000 SCF/yr

CAPITAL COSTS

Fixed Capital (includes installation)

1,700,000

OPERATING COSTS . Raw Materials (includes Oil) Utilities (Vendor Estimate)

114,625

Contingency (3% Fixed Capital)

51,000

Labor

3,800 6,600

Working Capital (20% Fixed Capital)

340,000

Maintenance (3% Fixed Capital) Lab Charges (10% Labor)

51,000 660

Supplies (10% Maintenance) Supervision (25% Labor & Maintenance) Overhead (30% Labor & Maintenance)

660 14,400 17.280

TOTAL Capital Costs:

2,091,000

TOTAL Operating Costs

TABLE A-8 Capital and Annual Operating Cost Data for: Supercritical Water Oxidation, Vendor B

PRIMARY OPERATING DATA

Shifts

Operations

Days 250 days/yr

1 shift/day

hr/yr hr/shift 2,000

1 operators/shift

Pink Water

Flowrate

No. of Operators

20 gpm 9,600 gpd

Initial Concentration Final Concentration 200 ppm

2,400,000 gpy

0.25 ppm

COST DATA

Capital Costs

Contingency

3 % Fixed Capital

Littles

Electricity

0.10 \$/kW-hr

Working Capital

20 % Fixed Capital

Natural Gas

6 \$/1000 SCF 0.01 \$/gal

Water

Direct Expenses

Operator Labor Maintenance 10 S/hr

3 % Fixed Capital

Supplies

10 % Maintenance 2 % Fixed Capital

Materials Lab Charges

10 % Labor

Indirect Expenses

Supervision

25 % Labor and Maint

Overhead

30 % Labor and Maint

Process Specific Calculations

Gas Requirements Reaction Fuel

300,000 85,000 SCF/yr

CAPITAL COSTS

Fixed Capital (includes installation)

1,750,000

OPERATING COSTS

Raw Materials

120,000 4,800

Contingency (3% Fixed Capital)

52,500

Utilitles (Estimate) Labor

20,000

Working Capital (20% Fixed Capital)

350,000

Maintenance (3% Fixed Capital) Lab Charges (10% Labor) Supplies (10% Maintenance)

Supervision (25% Labor & Maintenance)

Overhead (30% Labor & Maintenance)

52,500 2,000 2.000

TOTAL Capital Costs:

2,152,500

TOTAL Operating Costs

241,175

18,125

TABLE A-9 Capital and Annual Operating Cost Data for: Electron Beam, Vendor A

PRIMARY OPERATING DATA

Operations

Days

250 days/yr

hr/shift

Shifts

1 shift/day

hr/yr 2.000

8

No. of Operators

1 operators/shift

Pink Water

Flowrate

20 gpm

Initial Concentration

200 ppm

9,600 gpd 2.400,000 apy

Final Concentration

0.25 ppm

COST DATA

Capital Costs

Contingency Working Capital 3 % Fixed Capital

20 % Fixed Capital

Utilities

Electricity

0.10 \$/kW-hr

Other

10 % Electric

Direct Expenses

Operator Labor

10 \$/hr

Maintenance

1.5 % Fixed Capital 10 % Maintenance Supplies | 1 % Fixed Capital

Materials Lab Charges

10 % Labor

Indirect Expenses

Supervision Overhead 25 % Labor and Maint

30 % Labor and Maint

OPERATING COSTS CAPITAL COSTS

Fixed Capital (Includes installation)

1,400,000

Raw Materials Utilities (Vendor Estimate)

Working Capital (20% Fixed Capital)

Contingency (3% Fixed Capital)

280,000

42,000

Labor Maintenance (1.5% Fixed Capital) Lab Charges (10% Labor) Supplies (10% Maintenance)

Supervision (25% Labor & Maintenance) Overhead (30% Labor & Maintenance)

TOTAL Capital Costs:

1,722,000

TOTAL Operating Costs

94,750

14,000

13,200

20,000

21,000

2,000

2,000

10,250 12.300

TABLE A-10 Capital and Annual Operating Cost Data for: Electron Beam, Vendor B

PRIMARY OPERATING DATA

Operations

Days

250 days/yr.

hr/yr.

hr/shift

Shifts No. of Operators

1 shift/day 1.5 operators/shift 2,000

8

Pink Water

Flowrate

20 gpm

Initial Concentration

200 ppm

9,600 gpd

2,400,000 gpy

Final Concentration

0.25 ppm

COST DATA

Capital Costs

3 % Fixed Capital

UNittes

Electricity Other 0.10 \$/kW-hr

Working Capital 20 % Fixed Capital

10 % Electric

Direct Expenses

Operator Labor

Contingency

10 \$/hr

1.5 % Fixed Capital

Maintenance Supplies

10 % Maintenance

Materials Lab Charges

1.5 % Fixed Capital 10 % Labor

Indirect Expenses

Supervision Overhead

25 % Labor and Maint

30 % Labor and Maint

CAPITAL COSTS

OPERATING COSTS

Fixed Capital (includes installation)

2,600,000

Raw Materials Utilities (Vendor Estimate) 39,000 27,500

Contingency (3% Fixed Capital)

78,000

Labor Maintenance (1.5% Fixed Capital) Lab Charges (10% Labor)

30,000 39,000 3,000

3,000

17,250

Working Capital (20% Fixed Capital)

520,000

Supplies (10% Maintenance) Supervision (25% Labor & Maintenance) Overhead (30% Labor & Maintenance)

20,700

TOTAL Capital Costs:

3,198,000

TOTAL Operating Costs

TABLE A-11 Capital and Annual Operating Cost Data for: Carbon Adsorption with Off-site Incineration

PRIMARY OPERATING DATA

Operations

Days Shifts 250 days/yr 1 shift/day

hr/yr.

hr/shift

2.000

No. of Operators

0.2 operators/shift

Pink Water

Flowrate

20 gpm

Initial Concentration Final Concentration

200 ppm 0.25 ppm

9,600 gpd

2,400,000 gpy

COST DATA

Capital Costs

3 % Fixed Capital 20 % Fixed Capital Utilities

Electricity

Supervision

Overhead

0.10 \$/kW-hr

25 % Labor and Maint

30 % Labor and Maint

Other 10 % Electric

Direct Expenses

Operator Labor 10 \$/hr

Maintenance

Contingency

Working Capital

1.5 % Fixed Capital 10 % Maintenance

Supplies Materials Lab Charges

1.5 % Fixed Capital

10 % Labor

Process Specific Calculations

Explosive Adsorb

30 wt % Explosives Adsorbed 4,000 lb/yr

Carbon Required

13,333 lb

Cost of Carbon

Incineration and Shipping

OPERATING COSTS

Indirect Expenses

1.00 \$/16 1.2 S/Ib

CAPITAL COSTS

Fixed Capital (includes installation)

130,000

Raw Materials (including carbon) Utilities (Estimate)

15,283 2.000

Contingency (3% Fixed Capital)

3.900

Labor Maintenance (1.5% Fixed Capital) 4,000 1,950

Working Capital (20% Fixed Capital)

26,000

Lab Charges (10% Labor) Incineration and Shipping Supplies (10% Maintenance)

Supervision (25% Labor & Maintenance)

Overhead (30% Labor & Maintenance)

400 20,800 400 1,488

1.785

TOTAL Capital Costs:

159,900

TOTAL Operating Costs

TABLE A-12 Capital and Annual Operating Cost Data for: Carbon Adsorption with Off-site Thermal Regeneration

PRIMARY	OPERATING DATA
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Operations

250 days/yr Days

1 shift/day Shifts

0.2 operators/shift

Pink Water

Flowrate

20 gpm

9,600 gpd 2,400,000 gpy

initial Concentration

hr/yr.

2,000

Final Concentration

hr/shift

8

200 ppm

0.25 ppm

COST DATA

Capital Costs

Contingency Working Capital

No. of Operators

3 % Fixed Capital

20 % Fixed Capital

Utilities

Electricity 0.10 \$/kW-hr

Other 10 % Electric

Direct Expenses

Operator Labor Maintenance 10 \$/hr

1.5 % Fixed Capital

Supplies Materials

10 % Maintenance 1.5 % Fixed Capital

10 % Labor

Indirect Expenses

Supervision Overhead

Attrition Rate

25 % Labor and Maint

30 % Labor and Maint

Lab Charges

Process Specific Calculations

Explosive Adsorb Explosives Adsorbed Carbon Required

30 wt %

4,000 lb/yr

Cost of Carbon

85 % 1.00 \$/lb

Regeneration and Shiping

0.85 \$/lb

CAPITAL COSTS

13,333 lb

OPERATING COSTS

Fixed Capital (includes installation)

130,000

Raw Materials Utilities (Estimate) Labor

3,950 2,000 4,000 1,950

Contingency (3% Fixed Capital) Working Capital (20% Fixed Capital) 3,900

Maintenance (1.5% Fixed Capital) Lab Charges (10% Labor)

400 14,733 400

26,000

Regeneration and Shipping Supplies (10% Maintenance)

Supervision (25% Labor & Maintenance) 1,488 1.785 Overhead (30% Labor & Maintenance)

TOTAL Capital Costs:

159,900

TOTAL Operating Costs

TABLE A-13 Capital and Annual Operating Cost Data for: PACT/WAO

PRIMARY OPERATING DATA

Operations

Days

250 days/yr

hr/yr hr/shift

Shifts

1 shift/day

2,000

No. of Operators

0.2 operators/shift

Pink Water

Flowrate

20 gpm -

Initial Concentration

200 ppm

9.600 gpd

2,400,000 apy

Final Concentration

0.25 ppm

COST DATA

Capital Costs

Contingency

Working Capital

3 % Fixed Capital 20 % Fixed Capital UMMes

Electricity

0.10 \$/kW-hr

Natural Gas

6 \$/1000 SCF

Water

0.01 \$/gal

Direct Expenses

Operator Labor

10 \$/hr Maintenance

Supplies

2 % Fixed Capital 10 % Maintenance

Materials

2 % Fixed Capital

Lab Charges

5 % Labor

Indirect Expenses

Supervision Overhead

25 % Labor and Maint 30 % Labor and Maint

Special Materials

Carbon Usage

37,500 lb/yr

Carbon Cost

0.5 \$/lb

CAPITAL COSTS

OPERATING COSTS.

Fixed Capital (includes installation)

250,000.

Raw Materials Utilities (Vendor Estimate) 23,750

Contingency (3% Fixed Capital)

7.500

Labor Maintenance (2% Fixed Capital) 16,250 4,000 5,000

Working Capital (20% Fixed Capital)

50,000

Lab Charges (5% Labor) Supplies (10% Maintenance) 200 400

Supervision (25% Labor & Maintenance) Overhead (30% Labor & Maintenance)

2,250 2.700

TOTAL Capital Costs:

307,500

TOTAL Operating Costs

TABLE A-14 Capital and Annual Operating Cost Data for: Fluidized Bed Bioreactor

PRIMARY OPERATING DATA

Shifts

Operations

250 days/yr Days

1 shift/day

hr/yr hr/shift 2,000

No. of Operators

0.2 operators/shift

Pink Water

Flowrate

20 gpm

initial Concentration

200 ppm

9,600 gpd

2,400,000 gpy

Final Concentration

0.25 ppm

COST DATA

Capital Costs

Contingency Working Capital 3 % Fixed Capital

20 % Fixed Capital

Utilities

Electricity

0.10 \$/kW-hr

Natural Gas

6 \$/1000 SCF

Water 0.01 \$/gat

Direct Expenses

Operator Labor Maintenance 10 \$/hr

Supplies

3.4 % Fixed Capital 10 % Maintenance

2.8 % Fixed Capital Materials

Lab Charges

TOTAL Capital Costs:

5 % Labor

Indirect Expenses

Supervision Overhead

25 % Labor and Maint

30 % Labor and Maint

CAPITAL COSTS		OPERATING COSTS	
Fixed Capital (Includes installation)	290,000	Raw Materials Utilities (Vendor Estimate)	8.000 2.100
Contingency (3% Fixed Capital)	8,700	Labor Maintenance (3.4% Fixed Capital)	4,000 10,000
Working Capital (20% Fixed Capital)	58,000	Lab Charges (5% Labor) Supplies (10% Maintenance)	200 400
		Supervision (25% Labor & Maintenance) Overhead (30% Labor & Maintenance)	3.500 <u>4.2</u> 00
TOTAL Capital Costs:	356 <i>.7</i> 00	TOTAL Operating Costs	32,400

TABLE A-15 Capital and Annual Operating Cost Data for: GAC-Thermophilic Biological Process

PRIMARY OPERATING DATA

Operations

Days 250 days/yr

hr/shift

Shifts No. of Operators

1 shift/day 0.2 operators/shift hr/yr. 2,000

8

Pink Water

Flowrate

20 gpm

Initial Concentration

200 ppm

9,600 gpd

2,400,000 gpy

Final Concentration

0.25 ppm

COST DATA

Capital Costs

Contingency Working Capital 3 % Fixed Capital

20 % Fixed Capital

Utilities

Electricity

0.10 \$/kW-hr

Other 10 % Electric

Direct Expenses

Operator Labor

10 \$/hr

Maintenance

1.5 % Fixed Capital

Supplies Materials 10 % Maintenance

Lab Charges

is 1.5 % Fixed Capital s 10 % Labor Indirect Expenses

Supervision

25 % Labor and Maint

Overhead

30 % Labor and Maint

Process Specific Calculations

Carbon Required
Cost of Carbon

1,100 lb/yr 1.00 \$/lb

CAPITAL COSTS

Raw Materials

Fixed Capital (Includes installation)

142,000

OPERATING COSTS

3.230

Contingency (3% Fixed Capital)

Utilities (Estimate) Labor 2.500 4.000

Committee of the contract of t

4,260

Maintenance (1.5% Fixed Capital) Lab Charges (10% Labor)

Overhead (30% Labor & Maintenance)

2,130

Working Capital (20% Fixed Capital)

28.400

Inoculum (Vendor estimate)
Supplies (10% Maintenance)
Supervision (25% Labor & Maintenance)

5,000 400 1,533

TOTAL Capital Costs:

174,660

TOTAL Operating Costs

21,032

1.839

TABLE A-16 Capital and Annual Operating Cost Data for: **Large Aquatic Plants**

PRIMARY OPERATING DATA

Operations

Days

250 days/yr

hr/yr

hr/shift

Shifts

1 shift/day

2,000

8

No. of Operators

0.1 operators/shift

Pink Water

Flowrate

20 gpm

initial Concentration Final Concentration 200 ppm

9,600 gpd

2,400,000 gpy

0.25 ppm

COST DATA

Capital Costs

Contingency Working Capital 3 % Fixed Capital

20 % Fixed Capital

Utilities

Electricity

0.10 \$/kW-hr

Other

10 % Electric

Direct Expenses

Operator Labor

10 \$/hr

1.5 % Fixed Capital

Maintenance Supplies

10 % Maintenance 1 % Fixed Capital

Materials Lab Charges

Working Capital (20% Fixed Capital)

10 % Labor

Indirect Expenses

Supervision Overhead

25 % Labor and Maint

1,500

1,200

2,000

2,250 200

200

1,063

1.275

9,688

30 % Labor and Maint

OPERATING COSTS CAPITAL COSTS Fixed Capital (Includes installation) **Raw Materials** 150,000

4,500 Contingency (3% Fixed Capital)

Utilities (Vendor Estimate) Labor Maintenance (1.5% Fixed Capital) Lab Charges (10% Labor) Supplies (10% Maintenance) Supervision (25% Labor & Maintenance)

Overhead (30% Labor & Maintenance) **TOTAL Operating Costs** 184,500 TOTAL Capital Costs:

TABLE A-17 Capital and Annual Operating Cost Data for: **NitRem Process**

PRIMARY OPERATING DATA

Operations

Days

250 days/yr

hr/yr hr/shift

Shifts

1 shift/day

2,000

No. of Operators

1.4 operators/shift

Pink Water

Flowrate

20 gpm

Initial Concentration Final Concentration 200 ppm

9,600 gpd

2,400,000 gpy

0.25 ppm

COST DATA

Capital Costs

Contingency Working Capital

3 % Fixed Capital 20 % Fixed Capital

Electricity

0.10 \$/kW-hr

Other

10 % Electric

Direct Expenses

Operator Labor

Maintenance

10 \$/hr

3 % Fixed Capital

Supplies Materials 10 % Maintenance 1 % Fixed Capital

Lab Charges

10 % Labor

Indirect Expenses

Supervision Overhead 25 % Labor and Maint

30 % Labor and Maint

OPERATING COSTS CAPITAL COSTS

Fixed Capital (Includes installation)

Working Capital (20% Fixed Capital)

4,560,000

Raw Materials Utilities (Vendor Estimate) 32,400 58,000 28,000

Contingency (3% Fixed Capital)

136,800 912.000 Labor Maintenance (3% Fixed Capital) Lab Charges (10% Labor) Supplies (10% Maintenance)

Supervision (25% Labor & Maintenance)

Overhead (30% Labor & Maintenance)

136,800 2.800 2,800

41,200

49,440

TOTAL Capital Costs:

5,608,800

TOTAL Operating Costs